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STUDIES IN ISO-UREAS AND ISO-UREIDES

II. THE CONDENSATION OF ISO-UREAS WITH DIKETONES AND KETONIC ESTERS¹

By STEWARD BASTERFIELD² AND EDWARD C. POWELL³

Abstract

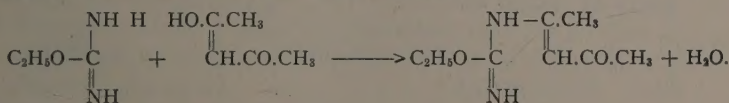
This investigation deals with the reaction of ethyl iso-urea with acetyl-acetone, oxalacetic ester, acetone-dicarboxylic ester, and acetyl-pyruvic ester. Several pyrimidines have been synthesised. So far, the condensation of acetyl-pyruvic ester has yielded only gums which could not be purified or converted into crystalline substances.

Introduction

The condensation of methyl and ethyl iso-ureas with β -oxy-acid esters to form pyrimidines was studied by W. M. Bruce (1). 2-Methoxy- and 2-ethoxy-4-methyl uracil were obtained by condensing methyl and ethyl iso-ureas with acetoacetic ester.

The present paper is concerned with the possibility of condensing ethyl iso-urea with acetyl-acetone, ethyl acetone-dicarboxylate, ethyl oxalacetate and ethyl acetyl-pyruvate.

Acetyl-acetone and ethyl iso-urea, on condensation, offer two possibilities of compound formation. If one only of the methylene hydrogens of acetyl-acetone were sufficiently active under the influence of the neighboring carbonyl groups, an open-chain compound would form:



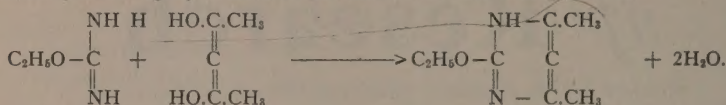
¹ Manuscript received August 1, 1929.

Contribution from the laboratories of the University of Saskatchewan, Saskatoon, Canada. This paper is based on a thesis presented by the junior author to the Faculty of Arts and Science, University of Saskatchewan, in partial fulfilment of the requirements for the degree of M.Sc.

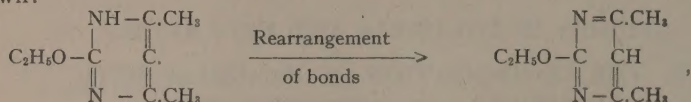
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If, however, both methylene hydrogens were sufficiently active, a further condensation would take place giving rise to a ring compound with the peculiarity of a highly unsaturated carbon in the fifth position:

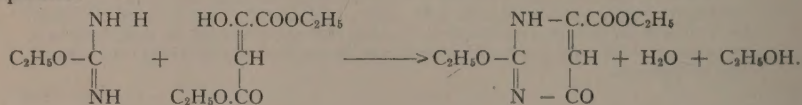


It is doubtful, however, if such a ring system would be stable enough to persist; it would probably rearrange to the more stable conjugated system as shown:

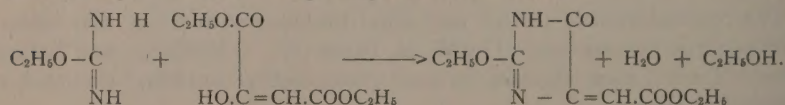


yielding a compound which should not show olefine properties.

The condensation of ethyl oxalacetate and ethyl iso-urea also presents two possibilities of compound formation. The reaction could be similar to that between acetoacetic ester and ethyl iso-urea (1), yielding a six-atom ring compound:

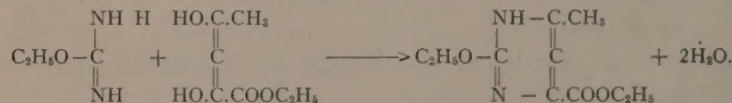


Alternatively, a five-atom ring compound could form:

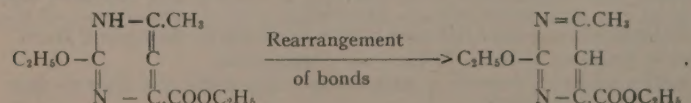


The two compounds are isomeric esters each containing an olefine bond, but should be readily distinguished since the first is related to uracil, and the second to parabanic acid.

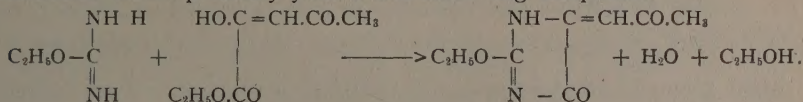
Ethyl acetyl-pyruvate and ethyl iso-urea also present two possible modes of condensation. They might condense in a similar fashion to acetyl-acetone and ethyl iso-urea, giving rise to a six-atom ring compound containing a highly unsaturated carbon atom in the fifth position:



This ring system would doubtless also rearrange to a more stable conjugated system as shown:

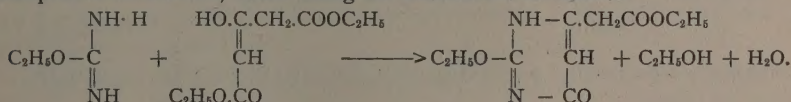


If, however, only one methylene hydrogen could bring about enolisation, the condensation would probably yield a five-atom ring compound:



These two possible compounds are not isomeric and could therefore be distinguished by analysis. Moreover the second one would possess a true olefine bond, and the first a closed conjugated system.

Ethyl acetone-dicarboxylate and ethyl iso-urea present only one possibility of compound formation, there being no alternative as shown:



Since there is no possibility of conjugation here the compound should show evidence of the presence of an olefine linkage between carbons 4 and 5.

The experimental study has shown that acetyl-acetone condenses with the substituted iso-urea in two stages. The product first formed was isolated and shown to be the open-chain compound ethyl iso-ureido-acetyl-acetone. It undergoes transformation in a few hours to the cyclic compound, 2-ethoxy-4-6-dimethyl-pyrimidine, which does not show the properties of an unsaturated compound, but reacts with bromine by substitution to give a monobromo derivative. Hence, as expected, the final product must be regarded as a stable conjugated ring structure.

The reaction between ethyl acetone-dicarboxylate and ethyl iso-urea proceeded very smoothly giving rise, as was anticipated, to ethyl 2-ethoxy-uracil-4-acetate. The structure and identity of this ester was established by its conversion to the acid, and the production from the acid by the elimination of carbon dioxide, of 2-ethoxy-4-methyl-uracil, a previously known compound. Further, the presence of an olefine linkage in the molecule was proved by the rapid absorption of one molecule of bromine to give a dibromo-derivative.

The condensation of oxalacetic ester with the substituted iso-urea took place very readily, but the isolation of a pure substance was rather troublesome. Analysis of the product obtained indicated that ring condensation had occurred, but whether the five or the six-atom system had been formed has not been ascertained. There are indications that the product analysed may be a mixture of isomers, but further work will be necessary to establish definite conclusions.

No product has been isolated from the reaction between ethyl-acetyl-pyruvate and the iso-urea. The reaction was vigorous but yielded an intractable gummy material. The purity and stability of acetyl-pyruvic ester and the optimum conditions for the condensation, are problems which will be studied further.¹

¹ The further study of these condensations has been temporarily suspended owing to the expiration of the period of the Bursary held by the junior author.—S.B.

Experimental

CONDENSATION OF ETHYL ISO-UREA WITH ACETYL-ACETONE

1. *Ethyl Iso-ureido-acetyl-acetone*, $\text{NH:C(OC}_2\text{H}_5\text{).NH.C(CH}_3\text{):CH.CO.CH}_3$.

Eight grams of ethyl iso-urea was mixed with its molecular equivalent of pure acetyl-acetone. The mixture formed a white solid in a few minutes, a distinct rise in temperature being noted. The solid was broken up with a glass rod, washed thoroughly with dry ether and dried in a vacuum desiccator. Melting Point $49^\circ\text{--}50^\circ\text{C}$. Yield, 50-60% of the theoretical.

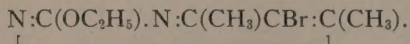
Analysis: N calculated for $\text{C}_8\text{H}_{14}\text{N}_2\text{O}_2$	16.46%,
Found	16.90, 16.73%.

2. *2-Ethoxy-4-6-dimethyl-pyrimidine*, $\text{N:C(OC}_2\text{H}_5\text{).N:C(CH}_3\text{).CH:C(CH}_3\text{).}$

Ethyl iso-ureido-acetyl-acetone was unstable and, on standing four to five hours in a vacuum, turned to a mush of crystals. The latter was dried in a vacuum desiccator for about a week, then broken up with a glass rod and washed thoroughly with ether. The treatment left a white substance which, on recrystallation from hot alcohol, produced a mass of fine white crystals. Melting point 162°C . (with decomposition). Yield, 20-25% of the theoretical.

Analysis: N calculated for $\text{C}_8\text{H}_{12}\text{N}_2\text{O}$	18.41%,
Found	18.37, 18.44%.

3. *2-Ethoxy-4-6-dimethyl-5-bromo-pyrimidine*,



One gram of 2-ethoxy-4-6-dimethyl-pyrimidine was dissolved in 30 cc. of glacial acetic acid and twice its molecular equivalent of bromine added very slowly. There was no disappearance of bromine and therefore no indication of an olefine linkage. After warming the solution under reflux for half an hour on an oil bath, a yellow crystalline mass was precipitated by the addition of water. The precipitate was dissolved in hot alcohol from which it separated on cooling in very fine white crystals. Melting point 196°C . The exact yield was not recorded.

Analysis: N calculated for $\text{C}_8\text{H}_{11}\text{N}_2\text{BrO}$	12.12%,
Found	11.94%.

CONDENSATION OF ETHYL ISO-UREA WITH ETHYL OXALACETATE

Five grams of ethyl iso-urea was mixed with its molecular equivalent of ethyl oxalacetate. The mixture reacted immediately, producing a yellow sticky gum and a very distinct rise in temperature. Within a period of one hour the gum, on standing, turned brown, purple, and finally black. After standing a month in a desiccator the black gum had become so sticky and

viscous that it could not be stirred with a glass rod. It was readily soluble in hot chloroform, and from the solution low boiling ligroin precipitated a chocolate-colored amorphous substance giving rise to a gum on drying.

The production of a gum may have been due to some impurity in the ethyl oxalacetate bringing about polymerization. A sample of ethyl oxalacetate was therefore fractionated and the first fraction after the boiling point became steady was collected and condensed with its molecular equivalent of ethyl iso-urea. A yellow slightly gummy mass was formed with a decided evolution of heat. This product, after standing several days and being washed with ether to remove all the gummy material, left a slightly yellow crystalline residue. This was dissolved in a mixture of hot alcohol and ether from which it separated on cooling in white crystals. Melting point 154°C. Yield, 50% of the theoretical.

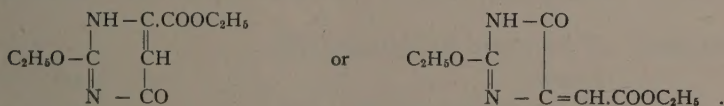
Analysis: N calculated for $C_9H_{12}N_2O_4$	13.20%,
Found	13.44, 13.44%.

Second and third fractions of ethyl oxalacetate, were also condensed with ethyl iso-urea. A brown, and a black gum, respectively, were formed. This seemed to indicate the presence of some impurity in the higher fractions of ethyl oxalacetate.

A second fractionation was performed and some of the lower-boiling fraction was condensed as previously with its molecular equivalent of ethyl iso-urea. A light violet crystalline mass was formed almost immediately, and a decided evolution of heat noted. After standing several days, the crystalline mass was broken up, washed several times with ether, and re-crystallised from hot alcohol from which it separated on cooling in white crystals. Melting point 149°C. The yield was about 60% of the theoretical.

Analysis: N calculated $C_9H_{12}N_2O_4$	13.20%,
Found	13.19, 13.35%.

The above nitrogen content indicates that ring condensation has taken place, but it has not been proved whether the product is a five or six-atom ring compound. The two possible compounds are isomeric and hence have the same nitrogen content:



The substances produced as described above are possibly mixtures of isomers in slightly different proportions. A mixture of the two products melted at about 155°C., a little higher than the first product (154°).

CONDENSATION OF ETHYL ISO-UREA WITH ETHYL ACETYL-PYRUVATE

Five grams of ethyl iso-urea was mixed with its molecular equivalent of ethyl acetyl-pyruvate, reaction taking place immediately with very distinct rise in temperature. The brown sticky gum formed, after standing a month

in a desiccator, had set to such an extent that it could not be stirred with a glass rod. No solvent could be found for crystallisation and hence further work was not continued.

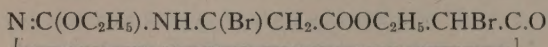
CONDENSATION OF ETHYL ISO-UREA WITH ETHYL-ACETONE-DICARBOXYLATE

1. *Ethyl 2-Ethoxy-uracil-4-acetate*, $\text{N:C(OC}_2\text{H}_5\text{).NH.C(CH}_2\text{.COOC}_2\text{H}_5\text{):CH.CO.}$

Five grams of ethyl iso-urea was mixed with its molecular equivalent of ethyl acetone-dicarboxylate. The reaction produced a yellow oil, with a very slight rise in temperature. After being warmed on a water-bath to 60°-70°C. for a few minutes and standing in a desiccator for several days, the oil solidified to a yellow crystalline mass. This mass was broken up with a glass rod, thoroughly washed with ether, and dissolved in hot alcohol from which it separated on cooling in white crystals. Melting point 112.5°C. Yield, 60% of the theoretical.

Analysis:	N calculated for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_4$	12.39%
	Found	12.26, 12.21%

2. *Ethyl 2-Ethoxy-4-5-dibromo-uracil-4-acetate*,



Two grams of ethyl 2-ethoxy-uracil-4-acetate was dissolved in chloroform and its molecular equivalent of liquid bromine added gradually to the solution. The rapid disappearance of bromine indicated addition at an olefine linkage. The chloroform was evaporated by means of a current of warm air and the residue, which remained as a brown amorphous mass, was taken up with cold water. It was separated by filtration and washed thoroughly with cold water to remove the excess bromine. The slightly yellow substance obtained was readily soluble in hot alcohol from which it separated on cooling in small white crystals. Melting point 175°C. The yield was practically quantitative.

Analysis ¹ :	N calculated for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_4\text{Br}_2$	7.26%,
	Found	7.40, 7.55%;
	Br calculated for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_4\text{Br}_2$	41.40%,
	Found	42.05, 41.90%.

Three grams of ethyl 2-ethoxy-uracil-4-acetate was also brominated in the cold in the presence of water. The procedure used was that of Behrend (3). A white powder was produced, but the yield was so small that further investigation was not continued.

¹ The method used in the determination of bromine in ethyl 2-ethoxy-4-5-dibromo-uracil-4-acetate was essentially that of I. Drogin and M. A. Rosanoff (2).

3. *2-Ethoxy-uracil-4-acetic acid*, $\text{N: C(OC}_2\text{H}_5\text{).NH.C(CH}_2\text{.COOH):CH.CO.}$

Two grams of ethyl 2-ethoxy-uracil-4-acetate was dissolved in about 150 cc. of 5% potassium hydroxide and refluxed over a low flame for half an hour. Sulphuric acid was then added to the solution until it was decidedly acidic. 2-Ethoxy-uracil-4-acetic acid separated out in soft feathery crystals when the solution was cooled in ice. The compound was filtered and washed thoroughly with cold water to remove sulphuric acid. The yield was practically quantitative.

Analysis: N calculated for $\text{C}_8\text{H}_{10}\text{N}_2\text{O}_4$	14.13%,
Found	13.97, 13.89%.

2-Ethoxy-uracil-4-acetic acid decomposes without melting and loses carbon dioxide when heated above 150°C. , forming 2-ethoxy-4-methyl-uracil. This was proved by taking about one gram of the substance in a large test-tube and heating in an oil bath at a temperature above 150°C. for fifteen minutes. The compound formed was readily soluble in hot alcohol from which it separated on cooling in shining needle-like crystals. Melting point 206°C. When mixed with a known sample of 2-ethoxy-4-methyl-uracil, there was no change in the melting point.

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THE SPECIFIC EFFECTS OF MONOCHROMATIC LIGHT ON THE GROWTH OF *PARMOECIUM*¹

By A. H. HUTCHINSON² and MIRIAM R. ASHTON³

Abstract

Paramoecium was irradiated with monochromatic light and it was found that rays of different frequencies have specific effects upon its growth. Certain frequencies in the red, the yellow and the near ultra-violet parts of the spectrum were found to stimulate growth; some as in the green and in the far ultra-violet beyond 3000Å retarded it, and even killed the organism at a very low intensity. Other frequencies retarded or stimulated growth during early exposure and later produced the reverse effects.

Introduction

Life obtains practically all of its energy from the sun in the form of light; this energy is in some cases stored by plants as food and is utilized later by both plants and animals, while in other cases it has a more direct effect. Ultra-violet light modifies the rate of growth and may cause death if the exposure is intense. Some disease-producing organisms are quite susceptible to the lethal effect, hence the use of ultra-violet light in therapeutics; for example, cancerous cells may be killed or their growth checked by its use. So, also, it may be used for sterilizing water and milk. Under certain conditions ultra-violet light stimulates growth and has a beneficial effect upon the development of bone; consequently it may be used for the prevention of rickets. Very recently it has been shown that new varieties of living forms may be induced by subjecting the parents to the action of X-rays during meiotic stages in their development, as in the case of the fruit fly and that of the tobacco plant. It is evident that ultra-violet light is of extreme importance; the difficulty in its use lies in the fact that experimental results are not constant, in other words, man's control of this force is far from complete.

Review of the Literature

Effect of Light on Protoplasm

The visible effects of the Schumann rays on protoplasm have been studied by W. T. Bovie (3) who attributes their violent destructive power to their general absorption by nearly all substances. The immediate effect on infusoria is a marked stimulation followed by cytolysis and, with sufficient exposure, death. The time required for death varies with the species and the individual organism.

With reference to localization of the physiological effects of radiation within the cell, Bovie (4) says that: "rays from widely separated regions of the spectrum, provided their ability to penetrate the organism is such that

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Contribution from the laboratories of the University of British Columbia, Vancouver, Canada, with financial assistance from the National Research Council of Canada.

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³ Graduate Student.

similar parts are radiated, produce similar physiological effects, regardless of difference in wave-length. Rays affect protoplasm at the place where they are absorbed, and observed physiological disturbances are the responses on the part of the organism to its injured protoplasm."

W. T. Bovie and G. A. Daland (6) established that exposure of *Paramoecium caudatum* to fluorite rays render them so extremely sensitive to heat that they are injured and even killed by an amount of heat which does not affect them when non-radiated.

In further experiments H. S. Forbes and G. A. Daland (8) found that *P. caudatum* were killed when exposed to ultra-violet light in the fluorite chamber. Ozone was present in the chamber but the fact that even on exclusion of this gas the organisms were killed showed the lethal character of the rays. It was also found that heat was more lethal when applied after than before radiation.

Charles Packard (14) exposed *P. caudatum* to radium radiations and described how the susceptibility of the organism varies with the temperature and with the permeability of the surface layer of the cell; also that β -rays increase the permeability of the surface layer, finally causing cytolysis. In this, β -rays resemble other forms of radiant energy. It is suggested that this increase in permeability following brief exposure is the cause of the acceleration in the division rate observed in *Paramoecium*.

The possible origin of the toxicity of ultra-violet light was studied by F. I. Harris and H. S. Hoyt (10) who prepared a pure culture of *Paramoecia* and a second culture suspended in a solution of aromatic amino acids. The suspension was irradiated directly, and the pure culture through a shield formed by a layer of the acid solution; in both cases the toxicity was decreased. The results are considered to be in harmony with the view that the susceptibility of protoplasm to ultra-violet light is conditioned by the selective absorption of the toxic rays by the aromatic amino acid radicals of the proteins. This view, however, does not exclude the possibility of other biochemical entities essential to life also showing a selective absorption for the toxic range.

According to D. M. Hughes and W. T. Bovie (12) *Paramoecium caudatum* undergo cytolysis when subjected to the action of ultra-violet rays for a sufficient length of time. Those organisms which do not cytolysed show no visible effects of irradiation except a peculiar stickiness of the outer layer of protoplasm which is sometimes observed. In his earlier investigations Bovie shows that ultra-violet rays used in the previous experiments are practically all absorbed in the cytoplasm of a cell about the size of *Paramoecium*. This fact suggests that the failure of the rays to inhibit cell division may be due to their inability to penetrate to the nucleus.

The same authors also find it possible to produce cytolysis in *Paramoecium* cells by a sufficiently long exposure to ultra-violet light from a quartz-mercury lamp (5). An exposure, insufficient to cause cytolysis, inhibits cell division, the organism gradually becoming extremely thin and transparent. With short exposures the latter condition is transitory and the organisms may recover

their normal state. Transitory inhibition is followed by a period of accelerated cell division sufficient to increase the number of individuals as compared to that normally developed in non-radiated controls. This is true, however, only if the inhibition is of short duration.

W. M. Baldwin (1) reports that X-radiation is more lethal to stained than to unstained organisms, and that the lethal effect seems to be due to the absorption of the stain by the cell nucleus. Since the nuclear membrane is normally impermeable to colloidal stains, he concluded that the X-rays lower the permeability, permitting the stain to diffuse readily into the nucleus.

Lethal Effect of Ultra-violet Light, Sterilization. Cancerous Growths.

Statistical records of the effect of measured monochromatic ultra-violet energy used to kill bacteria, show characteristic and similar curves at each wave-length studied. According to F. L. Gates (9), an appreciable amount of energy must be incident on the bacteria before any of them succumb and widely different intensities of energy are required to produce these curves at different wave-lengths. The results suggest that the reaction is reciprocally related to the absorption of ultra-violet energy by some sensitive element in the bacterial protoplasm. Further, the reciprocals of the curves are similar to the absorption curves of certain derivatives of the nucleo-proteins; this indicates that the lethal effect of ultra-violet light is due to the same reaction in both cases, and that the nucleo-proteins are related to cell growth and reproduction. This conclusion is supported by the known fact that the active agent of chicken tumors is associated with a nucleo-protein which, in all cases of sarcomatous cells gives a positive Feulgen reaction, pointing to the presence of thymonucleic acid. It is therefore possible that the lethal effect and the inhibition of cell division caused by ultra-violet light may be related to its action on the nucleo-proteins of the nucleus.

When a cell becomes cancerous the malignancy in it persists and is transmitted to the offspring, thus suggesting a profound modification of the nucleus (7). In all cases of sarcomatous cells, but in none of the normal fibroblasts examined, the Feulgen reaction for thymonucleic acid was positive.

The Anti-rachitic Effect of Ultra-violet Light

The ultra-violet light effective in the cure of rickets is reported by G. H. Maughan (13) to be located in the region between wave-lengths 3130 and 2650 Å. The curative effect of light of wave-lengths shorter than 2896 Å seems to be small, and that of wave-length 3130 Å nil. The results of careful analysis are that light of wave-length 2968 Å is the most effective for the cure of rickets, and that of wave-length 3024 Å is perhaps one-fourth as good.

R. M. Bethke and D. C. Kennard (2) in experimenting with chicks, eight weeks old, find that those placed under window-glass exhibit signs of severe leg weakness, while those exposed to direct sunlight or sunlight filtered through an ultra-violet glass continued to grow normally.

Hyperplasia of the parathyroid gland occurs in chicks fed on a diet deficient in calcium. Since calcium metabolism depends on vitamin D supplied in the diet (cod-liver oil) or by ultra-violet light, G. M. Higgins and C. Sheard (11) carried out experiments to determine the effect, on the parathyroid glands of chicks, of solar radiation filtered through blue, amber glass and vita-glass. They found that the absence of ultra-violet light, as in the case of the blue and amber screens, brought about hyperplasia which, however, could be partially checked by the addition of a small amount of cod-liver oil to the diet. The best development was found to take place under exposure to direct sunlight.

Description of Apparatus

The source of light used was a Cooper-Hewitt "Lab-arc". It was operated by means of an alternating current of 110 volts against a resistance of 12 ohms in series; under these conditions it functioned as a low pressure mercury arc. The exposures were continuous and lasted 24 hours; the intensity of the illumination was low, since a very narrow range of wave-length was used in each experiment.

The light was resolved by a Hilger Monochromatic Illuminator fitted with quartz lenses and prism, and reading directly in wave-lengths. The instrument was standardized from readings taken on the sodium D line. The organisms, *P. caudatum*, were placed in a quartz cell which fitted into a slot in front of the eye-piece of the Monochromatic Illuminator.

Description of Materials and Methods

Studies were commenced on *Paramoecium caudatum*, obtained from a pond adjoining a manure pile. It was found possible to obtain continuous division of the *Paramoecia* in a wild culture by the addition of 10 to 20 cc. of water from this pond at intervals of two or three days.

Owing to the large number of *Paramoecia* present, it was impossible to count them accurately until the culture was diluted. This was effected by agitating the wild culture by means of a glass rod, placing one cc. in each of three quartz receivers, and adding to each receiver three cc. of pond water. One receiver was exposed to light of a recorded wave-length, another to the full light from the "Lab-arc", at a distance of 0.5 meter, and the third kept in complete darkness in a box.

A control consisting of the same proportion of culture and pond water was kept in normal daylight.

Readings were taken for each exposure at the start and at intervals of four, six and 24 hours. The average count of ten drops from similar pipettes was taken, in determining the number of *Paramoecia* present. The solution was agitated before each reading as the organisms tended to aggregate at the bottom of the receiver.

The cultures were irradiated at room temperature, from 15° to 20°C. It was found that exposure of one of the cultures to the full illumination of the mercury arc raised its temperature approximately three degrees. This rise in temperature would normally have caused a slight increase in the rate of growth, whereas a decrease was observed in the culture.

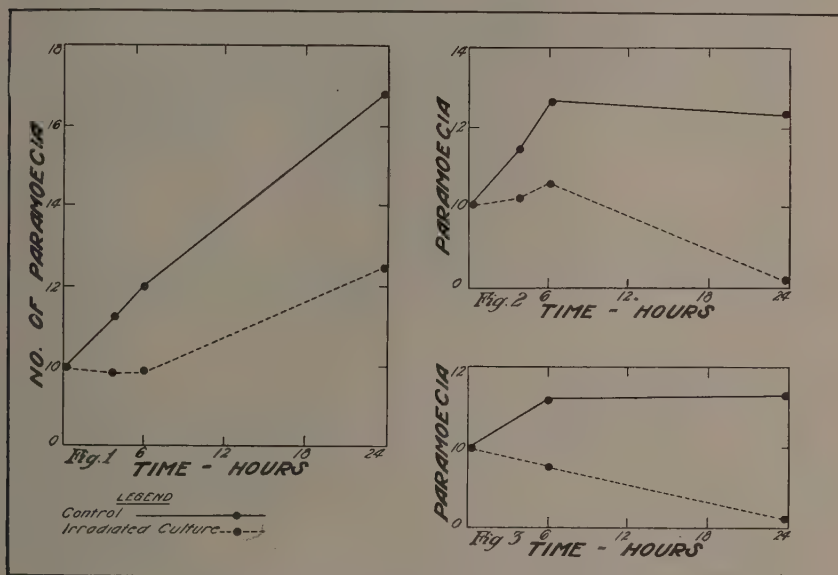
Relation between Growth of Control and Growth of Irradiated Culture

In each case the irradiated culture was compared with a control taken from the same colony of *Paramoecia* and at the same time. This comparison was necessary since the control itself may not be constant and may vary in its rate of growth from hour to hour. Numerous experimenters have shown in cultures of most unicellular organisms the existence of several phases of growth; the transition from one to the other is gradual, there being no definite limits. Generally, however, four stages may be recognized: (i) a primary lag period; (ii) a period of rapid growth, in which multiplication approaches a geometrical progression; (iii) a period of less rapid growth in which multiplication approaches an arithmetical progression, and the number of cells formed is approximately a function of the time; (iv) a secondary lag period. Priestley (15) has described these stages in connection with yeast and stated that the period of geometrical increase is the result of unimpeded cell division, while other phases of slower rate are caused by the effect of some retarding condition. Robertson (16) from an agreement between the growth curve and the chemical action curve which is dependent upon catalysis, deduces the auto-catalytic theory of growth. Whatever the explanation be, these variations in the rate of so-called "normal growth" make it necessary to compare the experimental culture with a control indicating the phase, that it would have reached normally.

Graphic Representation of the Effect of Experimental Conditions

Since the rate of growth of the control may vary as described above, it is difficult to represent by a graph the degree of stimulation or retardation caused by a change of conditions. A slowly growing culture may be more easily retarded or stimulated than a rapidly growing one; or the reverse may be the case. In order to represent truly all the significant variables, the rate of growth of the experimental culture should be represented on the same graph with the control culture. There are several methods of graphing. The more direct one is to use a separate figure for each experiment and to plot time as abscissae and number of *Paramoecia* per unit volume as ordinates; this is illustrated in Fig. 1, 2 and 3 for wave-length 2804 Å. Another method, used in all the other instances, consists in plotting as abscissae the "normal growth" of the control, in number of *Paramoecia*, and as ordinates the degree of stimulation or retardation measured as the positive or negative difference between number of *Paramoecia* per unit volume of the control and of the irradiated culture. The latter method represents the facts in a more concise

form; it is used in Fig. 16 to represent the effect of ultra-violet light of 2804 \AA upon the growth of *Paramoecium*. In the method used for the plotting of Fig. 1, the increase in number of *Paramoecia* bears a constant relation to time for each of the readings, four, six and 24 hours after starting the experiment. The number of *Paramoecia* in the control of Fig. 2 increases rapidly for the first six hours, but at a slower rate for the following 18 hours; in Fig. 3 the initial rate for the first six hours is less rapid than in the first two cases, and there is no increase for the last 18 hours. Obviously then, the experimental



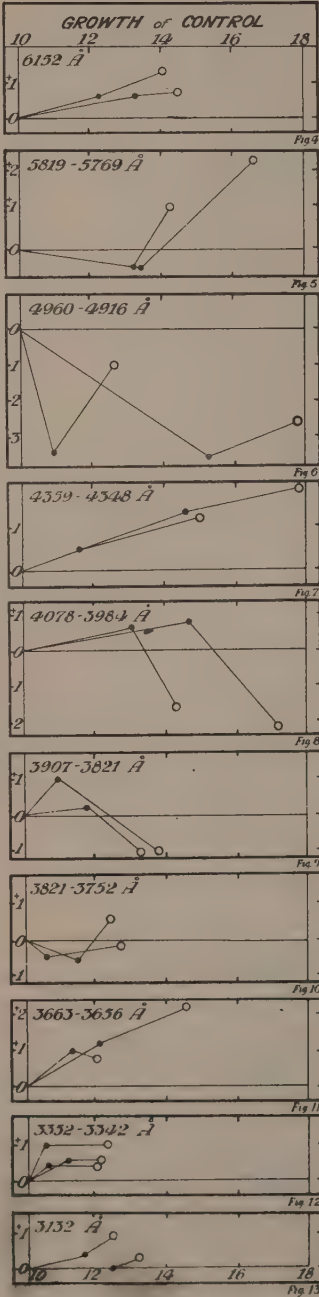
Effect of light ($\lambda = 2804 \text{ \AA}$) on the growth of *Paramoecia*.

Fig. 1 Control, at the first stage. Fig. 2 Control, at the second stage.

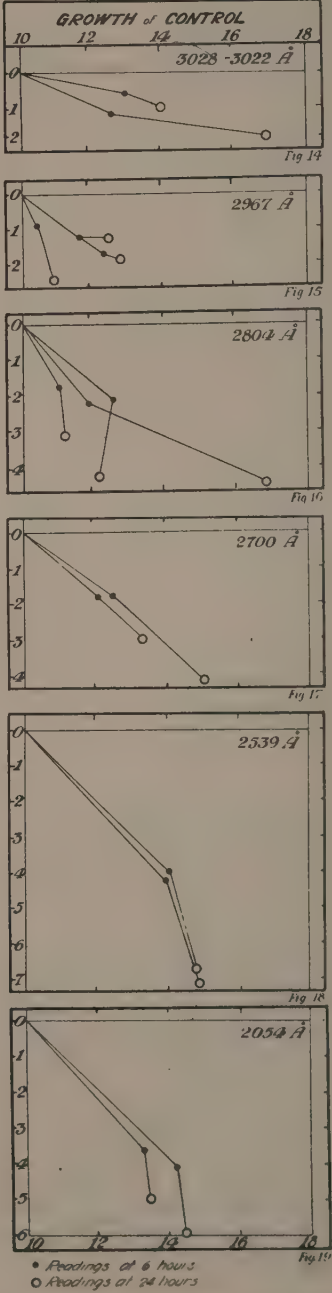
Fig. 3 Control, at the last stage.

controls were placed under observation at different phases of their normal growth. In the first case the irradiated culture does not multiply during the first six hours but during the following 18 hours its increase is approximately one-half that of the control. In the second experiment there is a small increase in number of *Paramoecia* in the irradiated culture during the initial 6 hours and a marked decrease after longer irradiation, while, in the third, decrease in number of *Paramoecia* is evident throughout the experiment. It would seem that in the first experiment the control has recently passed the primary lag period and, as shown by the curve, the effect of irradiation is to prolong this lag; in the other two experiments the control is taken at a phase approaching the second lag, the effect of irradiation being to accelerate the approach to this final stage.

STIMULATION + RETARDATION -



STIMULATION + RETARDATION -



• Readings at 6 hours
○ Readings at 24 hours

Effect of various selected rays of light on the growth of *Paramecium*.

Experimental Results

The specific effects of various selected rays of light on *Paramoecium* cultures are illustrated in Fig. 4-19; each culture is given as containing in its initial condition an average of ten cells per drop of liquid, determined from average counts of ten drops. The subsequent counts varied from four to 16 made on different days from different cultures. The average increase or decrease in number of *Paramoecia* was determined in the control exposed to room-light and in the culture exposed to monochromatic light; in some cases another culture was subjected to the full illumination of the mercury vapor light from the "Lab-arc" at a distance of 10 cm. The relative increase or decrease was then estimated using an original culture containing ten *Paramoecia* per drop as the basis. The growth of the control, in number of cells per drop, is represented as abscissae and the degree of stimulation or retardation similarly plotted as ordinates.

Fig. 4. $\lambda = 6152\text{\AA}$,

Includes two lines of low intensity in the red region of the visible spectrum. Exposure to this ray results in a constant and continued stimulation of intermediate degree.

Fig. 5. Range between $\lambda = 5819\text{\AA} - 5769\text{\AA}$,

Includes two lines of maximum intensity in the yellow region of the visible spectrum. At the end of six hours there is retardation in cultures exposed to these rays, but this later changes to stimulation which continues to the conclusion of the 24 hours.

Fig. 6. Range between $\lambda = 4960\text{\AA} - 4916\text{\AA}$,

This range includes a single green spectral line of rather low intensity. The effect of radiation is a very marked retardation during the first six hours, although this becomes less pronounced during the following 18 hours, but in no case does the growth equal that of the control. In some cases some *Paramoecia* are killed at first, but those which survive may multiply later.

Fig. 7. Range between $\lambda = 4359\text{\AA} - 4348\text{\AA}$,

Includes a line of intermediate intensity at the violet end of the visible spectrum; constant and rather marked stimulation throughout the 24-hour period.

Fig. 8. Range between $\lambda = 4078\text{\AA} - 3984\text{\AA}$,

Contains two lines of intermediate intensity at the lower limits of the visible spectrum; an initial stimulation of intermediate degree is produced during the first six hours, followed by a marked retardation.

Fig. 9 and 10. Ranges between $\lambda=3907\text{\AA}-3821\text{\AA}$ and $\lambda=3821\text{\AA}-3752\text{\AA}$,

Probably includes several lines of low intensity of this region. The results are quite erratic and difficult to understand. When stimulation is produced as the initial effect retardation follows, but, on the other hand, cases are obtained in which the reverse holds true. It is suggested that the two (or more) spectral lines included may possibly produce antagonistic effects, and that the seeming contradictory results may be due to slight differences in the setting of the instrument causing more intense illumination from one or the other line. At any rate, this region may be regarded as one of transition producing a variable effect; arbitrarily the results are separated into two groups represented in distinct graphs in Fig. 9 and Fig. 10.

Fig. 11. Range between $\lambda=3663\text{\AA}-3656\text{\AA}$,

Causes a decided stimulation which is less marked in slowly growing cultures.

Fig. 12. Range between $\lambda=3352\text{\AA}-3342\text{\AA}$,

Includes a mercury line of intermediate intensity in the near ultra-violet. There is a fairly marked stimulation during the first six hours which, however, does not continue. The rate of growth remains constant for the following 18 hours and the curve in each of three experiments runs parallel with that of the control.

Fig. 13. $\lambda=3132\text{\AA}$,

A line of intermediate intensity in the near ultra-violet. In contrast with the effect noticed in the range $3352-3342\text{\AA}$ this region has little effect for the first six hours, but stimulates growth slightly during the second period.

Fig. 14. Range between $\lambda=3028\text{\AA}-3022\text{\AA}$,

Region of intermediate intensity. *Paramoecia* under this exposure show an initial retardation in growth which, however, is temporary, and may not continue more than six hours. The degree of initial retardation seems to have some inverse relation to the period of its duration. The greater retardation is associated with a shorter period.

Fig. 15. $\lambda=2967\text{\AA}$,

A fairly intense spectral line. The retardation in growth caused by this line is continuous over the range of 24 hours; but the effect varies in degree.

Fig. 16. $\lambda=2804\text{\AA}$,

Illumination from two or three lines of low intensity, but there is a consistent and quite marked retarding effect on the growth.

Fig. 17. $\lambda=2700\text{\AA}$; *Fig. 18.* $\lambda=2539\text{\AA}$ and *Fig. 19.* $\lambda=2054\text{\AA}$,

These lines are in the far ultra-violet end of the spectrum and retard growth very markedly; for the greater part of the 24-hour period there is an actual decrease in the number of cells. It may be noted that the effect of

illumination with light of wave-length 2539\AA is somewhat greater than that of 2700\AA although the intensity is slightly less, and that the retardation caused by light of wave-length 2054\AA is the same as produced with that of 2700\AA , which is of much lower intensity.

The experimental results as plotted in Fig. 20 show that there is no direct relationship between intensity of radiation and the effect on the rate of growth of *Paramoecia*. This circumstance is strikingly illustrated by the effects on the cultures of the far ultra-violet light of wave-lengths 2700\AA and 2539\AA described above; also by the marked effect produced at wave-lengths 2054\AA , although the intensity of the light is low. It is also noteworthy that whereas light of $\lambda=4960-4916\text{\AA}$ and $3352-3333\text{\AA}$ have a similar intensity, the former retards growth while the latter stimulates it. An examination of Fig. 20 will reveal other instances.

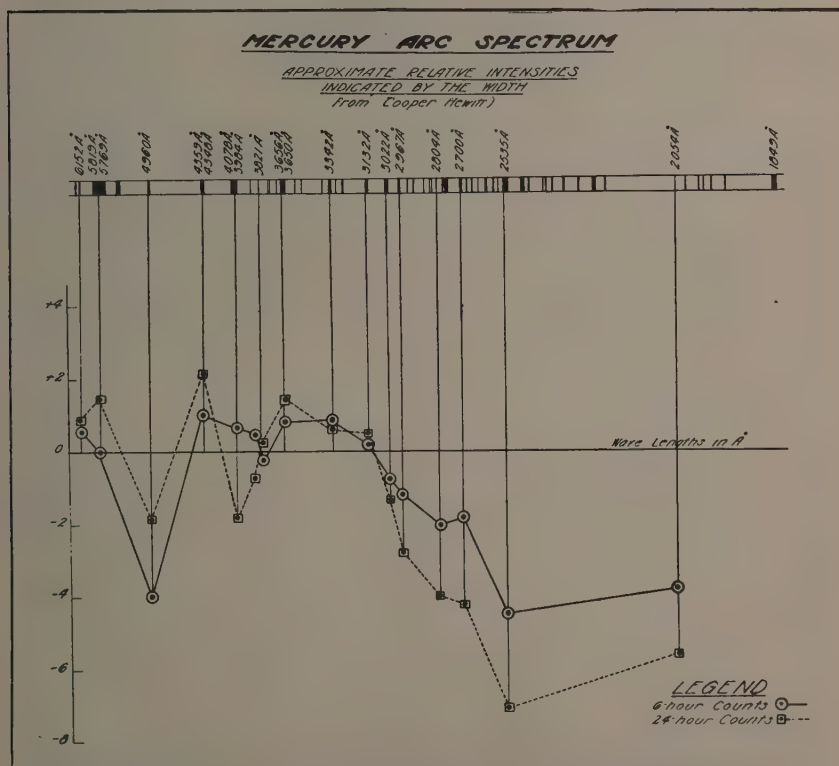


Fig. 20. Stimulation and Retardation of Growth in *Paramoecium* expressed as number of *Paramoecia* greater or less than in the control.

TABLE I

EFFECT OF VARIOUS WAVE-LENGTHS OF LIGHT ON THE RATE OF DIVISION OF *PARAMECIIUM* CAUDATUM

λ in Å	Number of <i>Paramecia</i> after four hours			Number of <i>Paramecia</i> after six hours			Number of <i>Paramecia</i> after 24 hours		
	Irradiated culture	Control	Difference	Irradiated culture	Control	Difference	Irradiated control	Control	Difference
6152	12.3 11.7	11.7 11.4	+0.6 +0.3	12.9 14.0	12.3 13.3	+0.6 +0.7	15.4 15.0	14.2 14.5	+1.2 +0.5
5819-5769	12.2 12.1	12.2 11.9	- +0.2	12.9 12.8	13.4 12.3	-0.5 +0.5	15.2 18.9	14.2 16.6	+1.0 +2.1
4968-4916	8.2 10.2	10.2 10.2	-2.0 -	7.3 10.9	10.9 15.2	-3.6 -4.3	12.0 18.0	12.9 20.8	-0.9 +2.8
4359-4348	10.9 14.0	10.8 13.3	+0.1 +0.7	12.1 16.1	11.5 14.6	+0.6 +1.5	16.1 22.2	14.9 19.2	+1.2 +3.0
4078-3984	12.7 11.9 10.2	13.2 11.7 11.0	-0.5 +0.2 -0.8	15.5 13.9 10.2	14.7 13.3 12.4	+0.8 +0.6 -2.2	15.0 12.8 10.9	17.2 14.3 12.6	-2.2 -1.5 -1.7
3821	9.6 - 12.5 -	11.2 - 10.7 -	-1.6 - +1.8 -	11.0 10.3 12.5 12.1	11.5 10.7 12.2 10.8	-0.5 -0.4 +0.3 +1.3	13.0 12.5 12.5 12.9	12.4 12.7 13.4 13.8	+0.6 -0.2 -0.9 -0.9
3663-3656	11.5 12.0 -	10.7 11.5 -	+0.8 +0.5 -	12.3 13.4 10.6	11.4 12.2 10.3	+0.9 +1.2 +0.3	12.9 16.5 11.5	12.1 14.4 10.6	+0.8 +2.1 +1.1
3352-3342	10.6 11.1 -	10.4 10.7 -	+0.2 +0.4 -	11.7 11.6 11.4	10.6 11.1 10.0	+0.9 +0.5 +1.4	13.4 12.7 12.5	12.4 12.2 12.1	+1.0 +0.5 +0.4
3132	11.5 11.6	11.5 11.2	- +0.4	12.2 12.4	11.8 12.4	+0.4 -	13.4 13.5	12.5 13.3	+0.9 +0.2
3028-3022	10.4 10.0	10.4 10.0	- -	11.2 12.9	12.5 13.5	-1.3 -0.6	15.2 13.1	16.9 14.1	-1.7 -1.0
2967	9.7 - 10.2	11.5 - 11.0	-1.8 - -0.8	10.6 9.7 10.9	11.7 10.5 12.6	-1.1 -0.8 -1.7	11.3 8.7 11.1	12.6 11.0 12.9	-1.3 -2.3 -1.8
2804	9.8 10.2 -	11.2 11.5 -	-1.4 -1.3 -	9.8 10.6 9.5	12.0 12.7 11.2	-2.2 -2.1 -1.7	12.5 8.1 8.2	16.9 12.3 11.3	-4.5 -4.2 -3.1
2700	- -	- -	- -	10.3 10.5	12.1 12.3	-1.8 -1.8	10.2 9.0	13.3 15.3	-3.1 -5.3
2535	- -	- -	- -	10.1 10.0	14.4 14.0	-4.3 -4.0	7.7 8.0	14.9 14.8	-7.2 -6.8
2054	- -	- -	- -	10.1 9.7	14.2 13.3	-4.1 -3.6	8.5 8.5	14.5 13.5	-6.0 -5.0

It is remarkable that the effect of irradiation in the case of each line used in the visible spectrum is such that the number of *Paramoecia* is greater at the end of 24 hours than after six hours, although the total action is stimulation in some cases and retardation in others. The same observation is true in the near ultra-violet while in the far ultra-violet the number of *Paramoecia* in the cultures is greater after six hours than after 24 hours of irradiation.

The results obtained in all the experiments are given in Table I as number of *Paramoecia* in the cultures after four, six and 24 hours irradiation. Each figure, representing an average of ten determinations is calculated for purposes of comparison, on the basis of ten organisms initially present in each culture.

Discussion of Results and Conclusions

There is a remarkable similarity between the specific effects of monochromatic light on the rate of division of *Paramoecium* as described in this paper and upon the growth of yeast (not yet published). The conclusion may be drawn that, within a given range, the response of animal and plant protoplasm to the effect of light is similar, although there is a difference of degree in the transition areas between stimulating and retarding rays.

Further evidence is necessary before a definite explanation of the nature and specificity of the effects can be given. It is evident, however, that intensity of radiation is not of primary importance, if indeed it bears any relation to the effect of one line as compared with that of another, and that it does not determine the direction of the effect. It seems reasonable to suggest that resonance phenomena may be involved and that certain particles in a colloidal or other state, possess vibration periods, such that their movements are affected by the specific frequencies of the radiant energy. On this basis subsequent effects may differ from the initial ones owing to associated changes in the colloidal condition.

Acknowledgments

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THE ALTERNATING CURRENT ELECTROLYSIS OF WATER¹

By J. W. SHIPLEY²

Abstract

An examination of commercial hot water heaters and steam generators of the electric water resistor type operating on alternating current shows that hydrogen and oxygen are generated within the electrode chamber. Current density is found to be the primary factor in the A.C. electrolysis of water at low voltages. At high voltages, arcing on the electrodes also results in the decomposition of the water. A critical current density exists for metallic electrodes below which electrolytic gases are not produced but above which all the current is utilized in decomposing the water into hydrogen and oxygen in accordance with Faraday's Law for continuous current. This critical current density varies with the nature of the electrode material, the temperature of the electrolyte and the frequency of the alternations: the higher the frequency the higher the critical current density. The storage capacity of the electrode for hydrogen and oxygen known as the "electrolytic capacity" is constant for copper but varies with the quarter-wave area for platinum and silver. At constant quarter-wave area the electrolytic capacity decreases to a minimum with increasing frequency. A difference in the phase for current and voltage is observed, the current leading the voltage. Wave distortion occurs in the case of platinum and copper electrodes. High voltage arcing by an alternating current produces a thermal decomposition of the water quite independent of A.C. electrolysis. The rate of decomposition by arcing is primarily dependent upon the rate of consumption of electrical energy. Hydrostatic pressure in the electrode chamber inhibits arcing. The application of the results to the design and operation of electric steam generators and domestic heaters is discussed, and the explosion hazard connected with the generation of electrolytic gas is also commented upon, a means being suggested for reducing the danger.

Introduction

The application of electric power in the production of steam by passing an alternating current directly through natural water by means of iron electrodes, whereby electrical energy is turned into heat and water into steam, has become very general wherever hydro-electric power is available. Particularly, in the provinces of Quebec, Ontario, and Manitoba, where coal has to be imported while hydro-electric power is locally available, this method of steam production is frequently found to be the only source of supply for large pulp and paper mills and other factories. When applied in conjunction with a steam accumulator, off-peak power may be used for the generation of the steam, and the accumulator provides a source of supply during the peak load hours of the electric generators, when the power is required for industrial purposes. This utilization of off-peak load makes it possible for the electric boilers to operate economically on power not marketable for other purposes.

Another application for steam generated by electric boilers during off-peak load is found in central heating systems where a large section of a city is provided with steam for heating purposes from a centrally located plant. Coal-fired boilers are used during the day and electric steam generators during the night.

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The use of the submerged electrode type of electrical hot water heater and steam generator was accompanied by the discovery that alternating electric current under certain conditions of boiler construction and operation produced considerable decomposition of the water into its elements. When it is highly diluted with steam the mixture of electrolytic gases produced is not explosive, but when the steam condenses the residual gases form an explosive mixture which must be considered as an explosion hazard. This explosion hazard depends upon the relative proportion of hydrogen and oxygen in the gaseous mixture, the volume of the gas and the possibility of ignition. The range of explosiveness of hydrogen and oxygen mixtures is so great that the danger of an explosion is not always prevented by the presence of steam in the gaseous mixture.

I. Generation of Explosive Gases in Heaters and Boilers

SERVICE HEATERS

A considerable number of hot water heaters of the bare, submerged electrode type are used in Canada and elsewhere for house heating purposes. The electrodes are suspended in an iron or steel electrode chamber into which the domestic water supply has free access. Single phase 60-cycle alternating current of 100, 220 or 550 volts flowing between the electrodes through the water generates the heat, the hot water circulating throughout the radiator system and returning to the heater. Should the temperature in the heater reach the boiling point, the steam formed drives the water off the electrodes into an expansion tank, and the current is interrupted. As the steam condenses the water flows back into the electrode chamber and the current is again established. The supply of heat is thus automatic, and under favorable conditions such a heater operates at a constant water level within the electrode chamber.

The complete demolition of an electric heater of this type together with the wrecking of the house in which it was installed suggested that the explosion causing this damage might have been due to an accumulation within the system of a mixture of hydrogen and oxygen, generated by the electrolysis of water. An inspection of several similar installations established the fact that gases of an inflammable and explosive nature were being generated within such heating systems.

GASES GENERATED IN SERVICE HEATERS

Samples of gases were secured from two water heaters. The first, a 550-volt single phase, 60-cycle installation, discharged gas continuously from the air relief valve at the rate of 10,000 cc. per day. The following analysis of the gas collected from this heater is typical:

Carbon dioxide.....	10.4%
Oxygen.....	1.4%
Hydrogen.....	49.8%
Nitrogen.....	38.4%

This gas was inflammable and, when mixed with 70% of air, explosive. After three months this heater was found to be generating gas of a similar composition and at about the same rate.

The second heater was a 220-volt, single phase, 60-cycle installation operating intermittently; it generated gas of the following composition at the rate of 2,000 cc. per 24 hours of operation.

Carbon dioxide.....	4.7%
Carbon monoxide.....	0.6%
Oxygen.....	1.0%
Hydrogen.....	54.5%
Nitrogen.....	39.2%

The gas was inflammable and, when mixed with air, explosive. Samples of gas collected during a period of three months had a similar composition, and the rate of generation was approximately the same.

Experiments on the generation of gases in this type of water heater were conducted by the author and Mr. A. Blackie of the National Testing Laboratories, Winnipeg, (28) in small model heaters designed to allow for the removal and exchange of the electrodes. Fig. 1 shows the apparatus used, and Table I contains the observed results for various electrodes. These experiments established the fact that single phase, 60-cycle, A.C. of either 110 or 220 volts generated gases in aqueous electrolytes and that these gases were generally of an explosive nature. The aqueous electrolyte used was water from the domestic supply of the city.

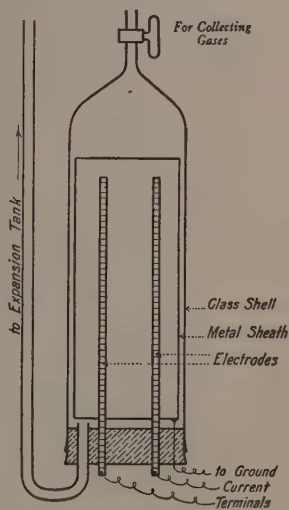


FIG. 1. Small Cast Iron Experimental Electric Water Heater.

GASES GENERATED BY ALTERNATING CURRENT

It is apparent from the composition of the gases generated, given in Table I, that their composition depends upon the nature of the electrodes used. The metals evolved very little, if any, gaseous hydrocarbons whilst the carbon electrodes produced a considerable percentage of these gases. During the process of electrolysis, all the electrodes were found to be attacked with the exception of the platinum. The carbon electrodes were mechanically disintegrated and the copper almost completely dissolved. Oxidizable metals absorbed the oxygen generated by electrolysis, forming oxides. This was particularly noticeable with copper, lead and aluminum which formed oxides or hydrated oxides as a sludge in the generator. This absorption of oxygen accounts for the low percentage of this gas and the high percentage of hydrogen in the mixtures collected.

TABLE I
ELECTROLYTIC GASES GENERATED BY A 60-CYCLE ALTERNATING CURRENT

Electrodes	Iron	Iron	Carbon	Carbon	Copper	Copper	Lead	Zinc	Aluminum	Nickel	Platinum
Voltage	220	110	220	110	220	110	110	110	110	110	Hydrogen and oxygen generated in equivalent proportions
Carbon dioxide	1.6	6.6	17.5	14.6	0.6	1.3	0.8	2.2	0.2	Explosive gases generated	
Oxygen	18.4	21.1	3.2	5.0	1.2	3.2	1.3	5.4	7.6		
Hydrogen	35.2	39.2	66.2	61.7	97.2	83.6	85.9	71.4	89.5		
Nitrogen	44.8	21.8	0.4	12.7	1.0	11.9	12.0	21.0	2.7		
Carbon monoxide			6.5	6.0							
Hydrocarbon gases			6.2								
Explosion	violent	violent	ignites	ignites	ignites	ignites	ignites	ignites	violent		violent
Approximate electrode surface exposed in sq. cm.	180	180	105	105	75	75	180	180	180	180	8
Gas collected in 24 hours in cc.	200	400	no record	no record	no record	no record	115	186	6000	no record	no record

NOTE: It was impossible to determine the current density as the electrode chamber was in continued surge with respect to the immersion of the electrodes due to the automatic control of this type of heater.

Oxygen also combined with the iron electrodes, but absorption was slower than with the metals just mentioned. The automatic control of this type of heater allowed the water to be evacuated into an expansion tank, where it cooled and redissolved atmospheric gases; as the electrode chamber of the heater cooled below the boiling point of water it was refilled with this aerated water. As the temperature rose again the water in the electrode chamber gave up its dissolved gases, and thus a fresh supply of oxygen, nitrogen and carbon dioxide was added to the mixture accumulating in the electrode chamber.

EFFECT OF LOWERING THE ELECTRICAL RESISTANCE UPON THE RATE OF GENERATION AND COMPOSITION OF THE GASES

It was deemed desirable to determine what effect a change in the nature of the electrolyte by the addition of certain salts might have upon the generation of gases. The following salts were chosen for this experiment: magnesium sulphate, sodium dichromate, potassium permanganate, sodium nitrate, sodium bicarbonate, sodium phosphate, sodium cyanide. They were considered the best adapted to inhibit the generation of gases. In every case, however, addition of these salts to the water in the electrode chamber increased the rate of generation of gases enormously. This rapid generation was due to the lowering of the resistance and the consequent increase in flow of the current through the electrolyte, providing a high current density on the electrodes.

EFFECT OF GROUNDING ON THE GENERATION OF GASES

Since all service installations are surrounded by a grounded metal shell in electrolytic contact with the electrodes through the electrolyte (tap water) the experimental generators just described were provided with metal sleeves connected to earth. In the case of the iron electrodes the generation of explosive gases was increased nine-fold by the introduction of the grounded shell, rising from 25 cc. in 12 hours to over 200 cc. evolved in the same time.

To simulate more closely the type of heater employed in service, a small cast iron model was operated on a 220-volt circuit with a wattmeter in series. The following is a typical analysis of the gas generated within this diminutive heater:

Carbon dioxide.....	13.0%
Oxygen.....	11.6%
Hydrogen.....	30.0%
Nitrogen.....	45.4%

This gaseous mixture was exploded by an electric spark.

It was found that the rate of evolution of gas depended upon the spacing of the electrodes and the relation of the electrodes to the shell, the current flowing, the temperature of the electrolyte and the depth of immersion of the electrodes. Moreover, the composition of the gaseous mixture was a function of the manner of operation of the system, namely, the surge between the electrode chamber, the radiating system and the expansion tank. The majority of these

variables are inter-dependent, and consequently the evaluation of the rate of evolution became very complicated. The maximum evolution appeared to take place just below the boiling point.

With water-cooled electrodes, (economically impracticable), consisting of iron pipes with water flowing through them, explosive gases were generated both upon the electrodes and the metallic sheath. Electrodes of different kinds of iron such as cast iron, mild steel and high carbon steel affected the composition of the gases very slightly.

EXPLOSIVENESS OF GASES

The explosiveness of the gases collected from the experimental heaters and service installations varied with the amount of inert gases present and with the oxygen content. The analyses of 22 gases are listed in Table II, arranged in order of increasing oxygen content. It will be noticed that in sample No. 7 the oxygen content is only 4.2% and the hydrogen 5.2%; this mixture gave but a slight explosion whereas all mixtures containing a higher percentage of oxygen and hydrogen exploded violently.

ELECTRIC STEAM GENERATORS

While conducting this investigation gas was observed escaping through water contained in the cup of an air valve attached to a steam radiator in the building in which the experimental water heater was installed. On applying a match, a sharp detonation occurred as each bubble broke. The radiators of this building were provided with steam from an electric steam generator in the basement operating on 60-cycle A.C. with 2,200 volts (8).

Two litres of gas was collected from this radiator and analyzed; it contained:

Carbon dioxide.....	0.6%
Oxygen.....	32.4%
Hydrogen.....	66.0%

Several of the radiators on the top floor of the same building became "air locked" and a sample of gas was removed from one of the cold radiators and analyzed. It had the following composition:

Carbon dioxide.....	0.4%
Oxygen.....	30.8%
Hydrogen.....	69.2%

It will be observed that hydrogen and oxygen occurred in these two samples in proportions approximately equal to those obtained by the electrolysis of water and similar to those producing an explosion of maximum violence.

EXPLOSIVENESS OF GASES IN RELATION TO STEAM

A sample of the explosive mixture was taken from the radiator mentioned above and 25 cc. placed in a wide eudiometer tube over mercury, with water in contact with the gas. The temperature was raised to 250°F.

(121°C.) and the gas permitted to stand in contact with the water for one hour, the pressure on the mercury manometer registering a little over two atmospheres. On passing an electric spark through the mixture, a violent explosion occurred completely wrecking the apparatus.

TABLE II
EXPLOSIVENESS OF GASES

Sample No.	1	2	3	4	5	6	7	8	9	10	11
Per cent composition											
Carbon dioxide	24.1	4.7	16.2	16.0	10.4	0.2	44.8	13.0	1.5	12.8	4.2
Oxygen	0.5	1.0	1.2	1.4	1.4	3.0	4.2	11.6	12.1	16.4	17.2
Hydrogen	18.6	54.5	26.8	16.6	49.8	15.5	5.2	30.0	11.5	6.0	18.0
Nitrogen	56.5	39.3	55.8	66.0	38.4	81.3	45.8	45.4	74.9	64.8	60.2
Explosiveness	—	—	—	—	—	—	X	X	X	X	X
Sample No.	12	13	14	15	16	17	18	19	20	21	22
Per cent composition											
Carbon dioxide	1.6	1.4	1.2	1.0	6.6	1.0	1.8	4.6	0.4	0.6	1.0
Oxygen	18.4	19.6	20.0	20.8	21.1	23.4	25.7	27.2	30.8	32.4	33.4
Hydrogen	35.2	4.8	42.8	3.1	39.2	19.4	4.6	20.7	69.2	66.0	62.3
Nitrogen	44.8	74.2	36.0	75.0	21.8	65.4	67.9	47.5	0.0	1.0	3.3
Explosiveness	X	—	X	—	X	X	—	X	X	X	X

(Explosive = X, Non-explosive = —).

The accumulation of gases in radiators or other cooling parts of a system operated with steam from an electric boiler must be considered extremely hazardous.

The explosiveness of such gaseous mixtures is determined by the proportions of hydrogen and oxygen present. The amount of water vapor present in the gases within the electrode chamber of a water heater was found to depend upon two factors, i.e., the quantity of other gases present in the chamber when ebullition began, and the hydrostatic pressure under which the system operated. When only a small quantity of permanent gases was in the electrode chamber the depression of the water was secured by the generation of a volume of steam almost equal to that of the liquid displaced, but as the chamber accumulated more and more of the permanent gases a smaller volume of steam was required to depress the water. With several of the gaseous mixtures listed in Table II the amount of steam generated would not have caused a sufficient dilution to prevent an explosion had an arc formed between the electrodes after displacement of the water from the electrode chamber. This would also be true even if the chamber were only partially filled with such gases.

Several experiments were made to determine the explosiveness of the gaseous mixtures listed in Table II under the conditions of water vapor saturation and pressure described above.

Finally a small experimental heater with the electrodes inserted from the top and without any vent being provided for the escape of the generated gases was set up and permitted to operate under a small hydrostatic pressure and low electrolytic resistance. The surging effect was very pronounced until a considerable volume of gas collected in the electrode chamber. After operating for about one hour the generator blew up wrecking the whole apparatus. As the explosion was accompanied by a flash it was presumably caused by the formation of an arc from the electrode when the electrolyte was depressed. The explosion took place at a temperature near the boiling point of water.

VENTING OF GASES

The accumulation of gases in the electrode chamber of service heaters has been recognized and automatic valves installed for their removal. Such valves are frequently set to remain open up to approximately 214°F. (101°C.), above which temperature they remain closed. The heaters, however, are actually operated under a pressure as high as two atmospheres at which pressure steam is generated and recondensed at 250°F. (121°C.). Consequently the temperature of the electrode chamber never drops to that at which the valve is automatically opened and therefore the accumulated gases cannot escape.

Such valves are also liable to become clogged by the accumulation of rust carried by the surging water in the electrode chamber. Such valves were frequently found to vent the accumulated gases only after vigorous tapping.

It is extremely hazardous to rely upon the automatic venting of the chamber gases and all installations of such water heaters should be provided with a water gauge glass whereby the accumulation of gases retained within the electrode chamber could easily be detected.

II. Current Density and the Law of Alternating Current Electrolysis

After establishing the fact that hydrogen and oxygen were being generated in hot water heaters and steam generators of the water-resistor type, the research was continued with the object of discovering the conditions under which the decomposition of the water took place. With these conditions known, it might be possible to construct electric hot water heaters and steam generators of this type and operate them without the production of explosive gases. With the able assistance of Mr. Chas. F. Goodeve the work was carried to a successful conclusion.

That an alternating current flowing across two electrodes through an electrolyte, decomposes water under certain conditions, and under other conditions causes no visible decomposition has long been known. In all cases the hydrogen and oxygen produced were considerably less than required by Faraday's Law (2), but no quantitative relationship between gas evolution and the current flowing was known. The possibility that the evolution of gas might be related to current density was advanced by Malagoli (2) who, however,

made no measurements. From the author's earlier investigations, with rectangular electrodes it was observed that the evolution of gas began as the current was increased, first at the sharp corners of the electrodes, and, at higher currents, along the edges. Thus with electrodes of platinum foil the first evolution of gas occurred on the corners when a current of 0.2 amperes was flowing while gas evolution began on the flat surfaces only when the current was increased to between three and four amperes.

IMPORTANCE OF THE SHAPE OF THE ELECTRODES

A consideration of the equipotential surfaces of electrodes immersed in a uniformly conducting medium discloses the fact that the current density is greatest on any projecting point or edge. The sharper this projecting point or edge, the greater the current density which may be many hundred times greater than on the flat surface. The exact value of this local current density is difficult to calculate but it is related to the curvature of the surface; the greater the curvature the greater the current density, and the latter is a minimum when the curvature is zero, that is, when the surface is flat. Electrodes in hot water heaters and steam generators should therefore be devoid of corners and edges and should expose a completely uniform surface, approximating as nearly as possible a flat surface. This can be most readily obtained by using cylindrical electrodes insulated at the top and bottom.

A measure of the relative current densities on an electrode is found in the rate of corrosion of the electrode. The higher the current density the more rapid is the corrosion. This variation of current density is found to have been totally neglected by early experimenters and by the manufacturers of commercial hot water heaters and boilers. Thus in the earlier forms of steam generators the lower ends of the cylindrical non-insulated electrodes corroded to pencil points and the electrodes rapidly became shorter. Edges and points also corroded away, the electrode *tending* to become of such a shape as to expose equipotential surfaces to the electrolyte. Equipotential surfaces, however, cannot be attained by the corrosion of the exposed projecting parts and consequently the destruction of the electrodes proceeded apace.

CRITICAL CURRENT DENSITY

Preliminary experiments (29) with electrodes designed to give uniform current density indicated that two identical cylindrical electrodes projecting from one flat insulator to another and separated by a distance relatively much larger than their diameters served the purpose. The cylinders were iron rods of a convenient diameter placed parallel to each other; the rubber insulating plates were also parallel to each other and their boundaries were at a distance much longer than the diameter of the electrodes. The electrodes were suspended in a beaker containing the electrolyte and provision was made for

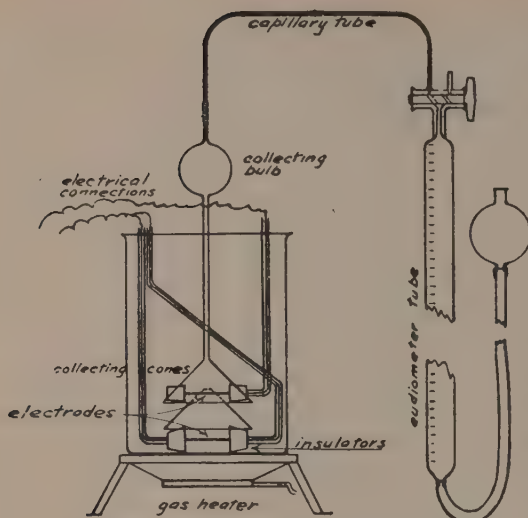


FIG. 2. Apparatus for determining the rate of electrolysis by alternating currents, showing the electrodes and gas-collecting apparatus. The temperature-controlling apparatus is not included in the diagram.

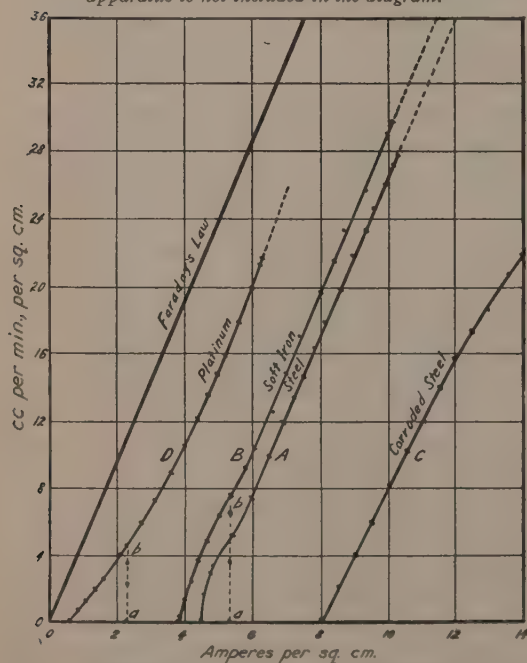


FIG. 3. Relation of rate of generation of electrolytic gases to current density, with platinum, iron and steel electrodes.

collecting the gases evolved by inverting a funnel over one electrode as shown in Fig. 2. The gases collected were analyzed for hydrogen by the copper oxide method to an accuracy of 0.1%.

With a dilute solution of sodium hydroxide (approximately 0.005 N.) as electrolyte and operating at the boiling point, gases were collected at gradually increasing current densities. Single phase, 60-cycle, current under 110 volts was used in this experiment. Small quantities of hydrogen and oxygen were evolved at low current densities but as soon as the bright polished surface of the iron electrodes became tarnished this evolution ceased. No trace of electrolytic gas was obtained until the current density reached 2.5 amperes per sq. cm. At this current density the rate of gas evolution was low and increased but slightly up to 3.5 amperes per sq. cm. beyond which value it increased proportionally to the impressed current. The gases evolved were violently explosive and contained two parts by volume of hydrogen to one of oxygen. Several determinations gave similar results and curves similar to that of B. shown in Fig. 3 were obtained on plotting the rate of gas generation against

current density. Above a certain current density value peculiar to the electrode surface, the rate of gas generation with alternating current was the same as that required by Faraday's Law for direct current electrolysis. The current density value at which electrolytic gas evolution began is the critical current density.

A temperature control attached to the apparatus kept the temperature regulated at 30°C. during electrolysis. Results obtained at this temperature are plotted in Fig. 3 and Fig. 4. A few experiments were carried out with acids and salts in the electrolyte but produced no marked difference in the position of the critical current density. The corrosion of the iron electrodes, however, was greater than in the sodium hydroxide solution.

THE LAW OF ALTERNATING CURRENT ELECTROLYSIS

The parallelism of the curves shown in Fig. 3 for iron and steel with that of the curve required by Faraday's Law may be expressed as follows: *Above the critical current density alternating current electrolysis follows the law of direct current electrolysis and may be made coincident with it by subtracting the critical current density from the current density used.* All of the current above the critical current density generates electrolytic gases which are liberated from the surface of the electrodes. If such a relationship holds for all electrodes then it becomes a law. Electrodes of several different metals were tried and curves similar to those for iron and steel were obtained.

The point at which gas evolution began was not always found to be the same for the same electrodes. On increasing the current density by small amounts it was found possible to pass the usual critical point without gas evolution beginning, the electrodes becoming darker than usual. When gas production did begin, however, the rate rose rapidly to that required for the current density impressed. This elevation of the critical point was particularly evident with copper. The dotted lines "a b" in Fig. 3 and Fig. 4 indicate the displacement observed in some instances. To avoid irregularities all rates of gas evolution were checked by determinations made with lowering current density.

On reducing the current density the evolution of gas was not regular in the close neighborhood of the critical point but proceeded in sudden bursts, each burst being accompanied by a color change on the electrode similar to that observed with the elevation of the critical point. The intervals of no gas production between the bursts increased as the critical current density was approached.

PLATINUM ELECTRODES

The relation of the rate of alternating current electrolysis to current density with platinum electrodes is shown by curve D in Fig. 3. The critical point was found to be at 0.70 amp. per sq. cm. and could be reproduced with accuracy. As with the soft iron an elevation of the critical point was frequently observed.

In the particular case shown in the figure this elevation amounted to 1.6 amp. per sq. cm. above the critical point, but it was found that the current density could, with care, be raised to 5.0 amp. per sq. cm. without evolution of gas. The metallic surface became coated with a deep gray substance, which was subsequently removed by the evolution of gas. The rate of evolution of gas coincided with the normal curve only after the coating had been completely removed. This coating was unlike platinum black, but was probably composed of finely divided platinum. The diameter of the electrodes decreased with use.

Although the curve with platinum could be easily reproduced with great accuracy, its lower part showed a decided departure from a straight line.

The significance of this will be dealt with in a subsequent paragraph.

SILVER ELECTRODES

Like platinum, silver electrodes showed a departure from a straight line near the critical current density (curve A, Fig. 4), but unlike platinum, this departure was small. The rate followed the law of alternating current electrolysis over a wide range. The critical current density required to be subtracted by this law was obtained by extrapolation from the curve. The actual critical current density was 1.6 amp. per sq. cm. while the extrapolated density was 2.3 amp. per sq. cm. No elevation of the critical current density was observed and the corrosion was negligible. The electrode surface became frosted in appearance and remained the same throughout.

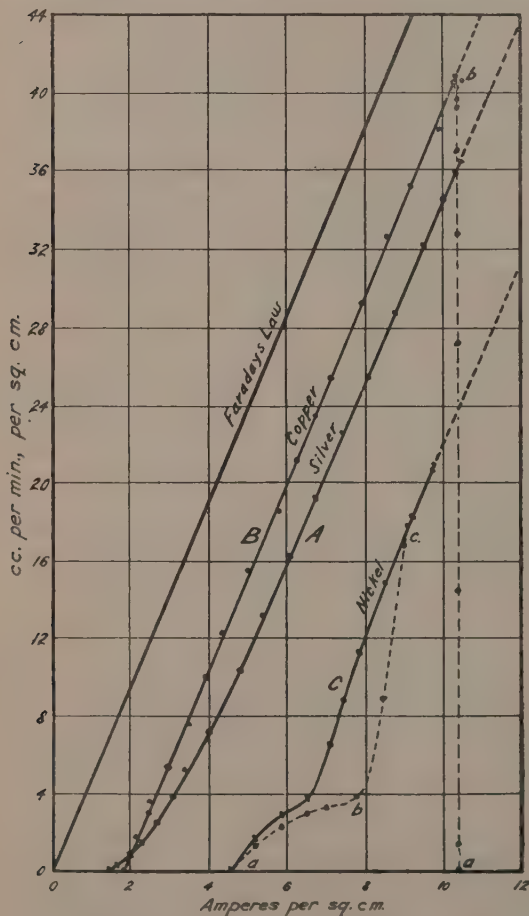


FIG. 4. Relation of rate of generation of electrolytic gases to current density, with copper, silver and nickel electrodes.

COPPER ELECTRODES

Copper gave a sharp critical point at 1.9 amp. per sq. cm., and a perfectly straight line curve throughout the range (curve B, Fig. 4.). On raising the current density from zero by small steps the usual critical point was passed without evolution of gas, the electrode becoming spotted with orange and black patches, and finally becoming completely black. The orange substance was likely cuprous oxide and the black, cupric oxide.

The critical current density was elevated to 10.2 amp. before evolution commenced. The black coating was rapidly removed by the gas, and the rate of evolution rose at constant current density as shown by the part "a b" of curve B in Fig. 4. The point "b" was reached only when the black copper oxide was all removed, after which the curve B was obtained with the clear copper surface. The presence of oxides of copper evidently has a more marked influence on the critical current density than the oxides of other metals.

NICKEL ELECTRODES

The rate of alternating current electrolysis for nickel electrodes did not follow the law at low current densities (curve C, Fig. 4). On increasing the current density above the critical point, the rate followed the dotted line "a b c," the normal curve C being obtained with decreasing current density. This may be a type of elevation of the critical current density. The departures from the straight line in the lower part of the curve may be accounted for by a variation in the thickness of the surface oxide-coating with the rate of gas evolution. A decided break occurred at a rate of approximately 3.5 cc. per minute. The corrosion of the electrodes was appreciable, but they remained a deep black throughout the measurements.

ALUMINUM ELECTRODES

A point below which no gas was evolved for aluminum electrodes could not be found, and the critical current density, if existing, must lie below 0.01 amp. per sq. cm. It was found impossible to obtain rate-current density curves, owing to the large changes of resistance and to the corrosion of the electrodes. Due to the chemical action of sodium hydroxide on aluminum, 0.5 N. sulphuric acid was substituted as the electrolyte.

THE THEORY OF A. C. ELECTROLYSIS OF WATER

The establishment of the law for A. C. electrolysis, by relating the rate of evolution of electrolytic gas (two volumes of hydrogen to one of oxygen) to current density above the critical point, led to the consideration of the mechanism of the electrolysis. No contribution of importance to the theory of this mechanism appears to have been made with the exception of that of Malagoli (2). His theoretical considerations were not based on quantitative evidence, but nevertheless have proved to be surprisingly in accordance with

observations. Apparently no notice has been taken of his contribution. Attempts were made by Mengarini (2) to develop a theory to account for the difference between A. C. and D. C. electrolysis, but his conclusions do not seem compatible with our results.

An alternating current being a series of equal and opposite direct currents should liberate *on the electrodes* its equivalent of hydrogen and oxygen according to Faraday's law. One ampere of direct current in one minute produces 10.4 cc. of electrolytic gas at standard conditions, in accordance with Faraday's law. As the ammeter reading of an alternating current is 1.11 times the average current, and as the average current is the electrochemical current, one ampere of an alternating current as read from the ammeter, should theoretically produce 9.42 cc. per minute. One electrode should produce 4.71 cc. of electrolytic gas per minute.

This can be represented by the equation,

$$R = 4.71 I_F \quad (1)$$

and by the curves shown in Fig. 3 and Fig. 4. In all cases in this research it was found that the alternating current produced less gas than required by Faraday's law. The rate of evolution was found (a) to be a function of the current density, when the current density was maintained uniform over the surface of the electrode, (b) to increase with the increasing current density above the critical point, and (c) to follow with few departures a straight line curve parallel to Faraday's law. The critical point was found to depend on the metallic nature of the electrode, the coating on the surface and the temperature (29).

Consider a metallic electrode, with an area exposed to the electrolyte of one sq. cm. immersed in an alkaline solution and an alternating current (Fig. 5) passing through the electrode, the solution and a second electrode. The current commences at the point A and decreases to zero at O. (If the current commences at any other point an equilibrium, in which the current may be considered as starting at the point A, is shortly reached as in ordinary alternating theory).

Part of the current may be stored by the electrostatic capacity effect between the charged ions and the electrode, an effect known to exist at low voltages, but as the current is induced by a voltage above the decomposition voltage, and is in this case positive, it discharges its equivalent in hydroxyl ions. Two discharged hydroxyl ions unite to form water and atomic oxygen. Part of the oxygen may combine with the metal of the electrode to form an oxide of the metal and part, either in the atomic or molecular condition, may be adsorbed on the surface or absorbed in the surface layer.

The remainder, if any, will form molecular oxygen and pass off from the electrode. The quantity that is absorbed, by combination or otherwise, depends on the metallic nature of the electrodes, the nature of the surface, temperature, etc., but independent, except in certain cases, of current density or voltage.

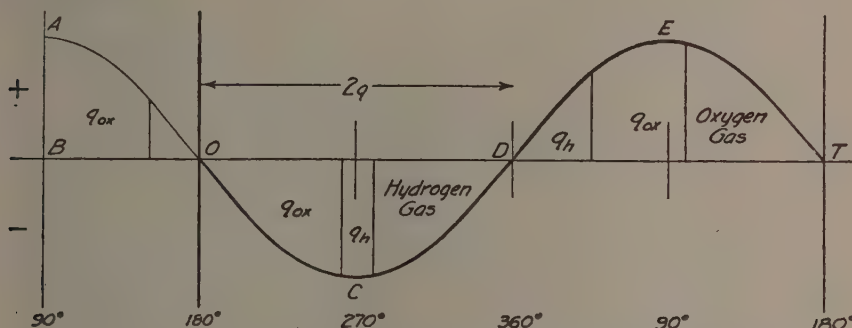


FIG. 5. Diagrammatic representation of the relation of the quantity of gas produced by an alternating current, to the electrolytic capacity of the electrode surface.

If the nature of the surface and the temperature is constant, the quantity which can be absorbed is constant and can be measured by the coulombs which produce it. This quantity is designated q_{ox} . The quantity of electricity that passes during the quarter-wave, that is the area OAB, is designated by q coulombs. The quantity of oxygen liberated from the electrodes, again measured in the coulombs that produce it, is equal to $q - q_{ox}$. At the point O the electrode is stored with oxygen and is producing a back electromotive force.

The current is reversed and hydrogen is discharged on the electrode. A quantity of hydrogen equivalent to q_{ox} will react with the oxygen stored from the last quarter-wave to reproduce water. The electrode will then be in its original condition, that is, electrically neutral. A quantity of hydrogen designated by q_h will combine with the metal, be adsorbed on the surface, or absorbed in the surface layer as with the oxygen and the remainder, if any, will form molecular hydrogen and pass off from the electrode. When the point D is reached the quantity liberated will be,

$$2q - (q_{ox} + q_h).$$

Owing to the high voltages sometimes occurring, the actual mechanism may be complicated by the discharge of metallic ions, such as sodium ions, but the resultant will be the same as above.

Similarly, in the half-wave DET, oxygen is discharged, a quantity q_h will neutralize the hydrogen of the previous half-wave and a quantity q_{ox} will be absorbed by the electrode. The quantity liberated will be equal to

$$2q - (q_h + q_{ox}).$$

Representing $(q_h + q_{ox})$ by $2Q_0$ we have as the electrochemical equivalent of the total quantity of electrolytic gas produced, in the cycle from O to T, the difference $4q - 4Q_0$.

With a current of frequency "f" the quantity produced in one second will be equal to $4fq - 4fQ_0$, and in one minute $240fq - 240fQ_0$. The quantity $240fq$ is the total quantity of electricity that has passed, which will be the average current multiplied by the time; that is, in one minute $60 I_1/1.11$ coulombs, where I_1 is the current per sq. cm. of electrode surface from the ammeter reading. From Faraday's law, one coulomb will liberate 0.174 cc. of electrolytic gas, or 0.087 cc. on one electrode. Therefore the volume "R" of gas liberated at standard conditions, per minute, per sq. cm., will be represented by

$$R_1 = 0.087 \left(\frac{60 I_1}{1.11} - 240fQ_0 \right)$$

or

$$R_1 = 4.71 (I_1 - 4.44fQ_0) \quad (2)$$

Thus we have an equation of alternating current electrolysis.

The value of f and Q_0 being constant and independent of the current, the rate plotted against the current (current density in this case) gives a straight line curve with a slope of 4.71, which is the slope of Faraday's law.

CRITICAL CURRENT DENSITY AND THE LAW OF ALTERNATING CURRENT ELECTROLYSIS

From equation 2 it is seen that when the current density is less than $4.44fQ_0$ (which is $1.11 \times 4fQ_0$), R_1 becomes negative. Actually R_1 becomes zero, the value of Q_0 not being fully satisfied. No resultant decomposition will take place until the current density exceeds the value of $4.44fQ_0$. This point is the "critical current density" and is represented by,

$$I_c = 1.11 \times 4fQ_0. \quad (3)$$

Substituting in equation 2

$$R_1 = 4.71 (I_1 - I_c), \quad (4)$$

which is the law of alternating current electrolysis as derived empirically (*vide*).

III. Frequency and Alternating Current Electrolysis

Experimental work by Maneuvrier and Chappuis (2) and by Marsh (2) has shown that the rate of electrolysis decreases with increase in frequency. They found (in their own experiments) that when the frequency was lowered gas evolution began. Malagoli (2) from theoretical considerations concluded that the mass of the products of electrolysis should vary inversely with the frequency. Quantitative determinations on the rate of electrolysis of water by an alternating current at different frequencies do not, however, appear to have been made.

Experiments were therefore carried out to determine the relation of A.C. electrolysis and the electrolytic capacity to the frequency of the alternations.

APPARATUS FOR DETERMINING RELATION OF FREQUENCY

The apparatus employed in this part of the research was essentially the same as used previously but with certain mechanical improvements to facilitate rapid and more accurate measurements. The principal of these was the introduction of a two-pole double-throw switch of a special design by which the electrodes could be instantly replaced in the circuit by a variable resistance, which was balanced to equal the resistance of the cell. This allowed the current to be fixed at any point and the generator adjusted to the load before the introduction of the cell, which adjustment was particularly necessary when heavy loads were used. In addition the continuous passage of current maintained the temperature constant and therefore the resistance of the controlling rheostats. Changes in the resistance of the cell, if any, were indicated by changes in the balanced resistance. The alternating current was supplied at frequencies below 60 cycles by a four-pole General Electric Alternator and above 60 cycles by a twelve-pole Holtzer-Cabot Motor Generator Set. The complete current measuring system was calibrated by a Kelvin Balance over the range of frequency and current used.

PLATINUM ELECTRODES

Experiments were performed with platinum wire electrodes of length 4.18 cm. and diameter 0.075 cm. in an electrolyte of normal sodium hydroxide solution, maintained at 30°C. Operating at constant frequency the system was adjusted to the upper limits of its current capacity and the rate at which gas was evolved at this current density was determined. The current was then lowered by definite steps and the rate of gas evolution determined for each step until gas ceased to be evolved. In this way the elevation of the critical point was avoided. This elevation is due to the formation of a grey substance (probably finely divided platinum) on the electrode surface, which thereby increased enormously the electrolytic capacity. Eight series of experiments were carried out at different frequencies between twenty and three hundred cycles per second. The rate of production of electrolytic gases by an alternating current at these frequencies, in cc. per min., from one electrode, corrected to standard conditions and divided by the area of the electrode, is shown in Fig. 6, plotted against the current density in amperes per sq. cm. of electrode surface.

It was remarkable that in the above experiments the platinum wire suffered considerable corrosion or loss of platinum. Fine platinum wires were found to wear completely away after a short time. A similar phenomenon was observed by Ruer (26). The corrosion on the electrodes used in the experimental work shown was very uniform and corroded electrodes were found to give almost exactly the same results as fresh electrodes.

At low frequencies the curve of alternating current electrolysis was found to be parallel to the curve of direct current electrolysis, except near the critical point, over a wide range of current densities. The critical current density

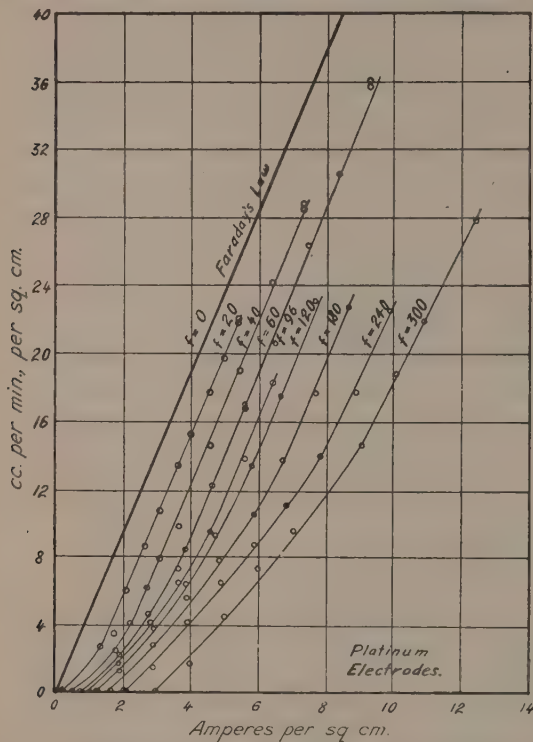


FIG. 6. Relation of current density to rate of generation of electrolytic gases by an alternating current at different frequencies, with platinum electrodes.

to be subtracted to make the curves coincident with Faraday's Law can be obtained by extrapolation of the curves to the axis. As the frequency was increased the departure near the critical point also increased and gas generation commenced at an increasingly higher current density. The experimental results indicate that the rate of A.C. electrolysis follows the law stated above at frequencies up to about 200 cycles provided that the current density exceeds a value approximately equal to 0.05 times the frequency. From the results shown it appears that this also holds true at frequencies up to 300 cycles, but the accuracy of the apparatus was limited over this range.

COPPER ELECTRODES

Experiments were performed with copper electrodes of length 3.14 cm. and diameter 0.102 cm. under the same conditions and at the same frequencies as with platinum. Considerable difficulty was encountered in obtaining consistent results at the same frequency owing to the formation of copper oxide on the surface. These patches of copper oxide, even when small, had a pronounced effect on the electrolytic capacity, and the curve obtained with an electrode in this condition lay to the right of the curve obtained with a polished copper electrode. Consistent results at low frequencies, and a minimum value for the electrolytic capacity, were eventually obtained by a preliminary cleaning of the electrode by evolving gas from it at a high density of 60-cycle current. The constant frequency curves were then taken at decreasing current densities, commencing as before at the upper limit. The

results were reduced to the same basis as for platinum and are shown in Fig. 7. When the rate of gas production became less than about three cc. per min., it was invariably found that the evolution would suddenly cease at constant current density, and the electrode would at the same time change from a bright copper color to a black. Accurate investigation of the region of the critical point was thus impossible. Complete avoidance of the formation of the oxide film at high frequencies was also found impossible, and the curves shown in Fig. 7 are typical of a number obtained. The corrosion of the electrodes was very rapid and they had to be replaced repeatedly throughout these experiments.

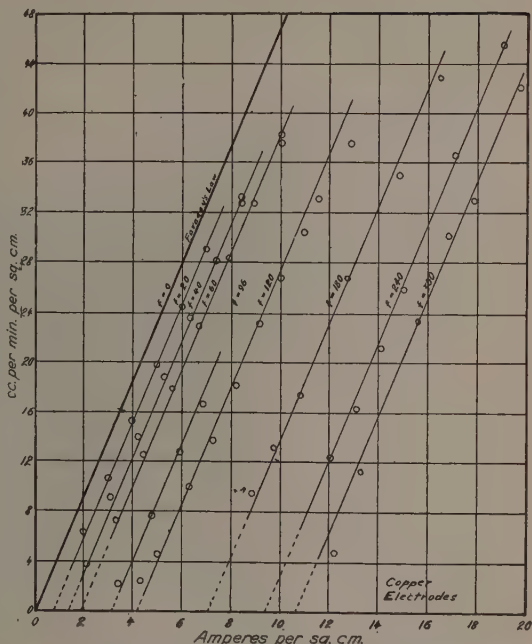


FIG. 7. Relation of current density to rate of generation of electrolytic gases by an alternating current at different frequencies, with copper electrodes.

As is seen from the curves, copper is a striking example of the law of A. C. electrolysis. The curves shown were drawn with a straight-edge parallel to the curve of Faraday's Law and all the points representing the experimental results lie very closely on these lines. This signifies that the electrolytic capacity is independent of the current density. The slight departures seen in the upper parts of some of the curves in Fig. 7 were not general and can be attributed to experimental error at the high rates of gas evolution. The relation of the electrolytic capacity to frequency cannot be obtained from these curves owing to the presence of oxides at high frequencies. The method of its determination is given in a succeeding paragraph.

SILVER ELECTRODES

Experiments were performed with silver electrodes of length 1.57 cm. and diameter 0.102 cm., under the same conditions and at frequencies of from 5 to 250 cycles. Consistent results were obtained without difficulty and no evidence of elevation of the critical point was observed. The corrosion of the electrodes was negligible. The results were reduced in the same way and plotted as shown in Fig. 8.

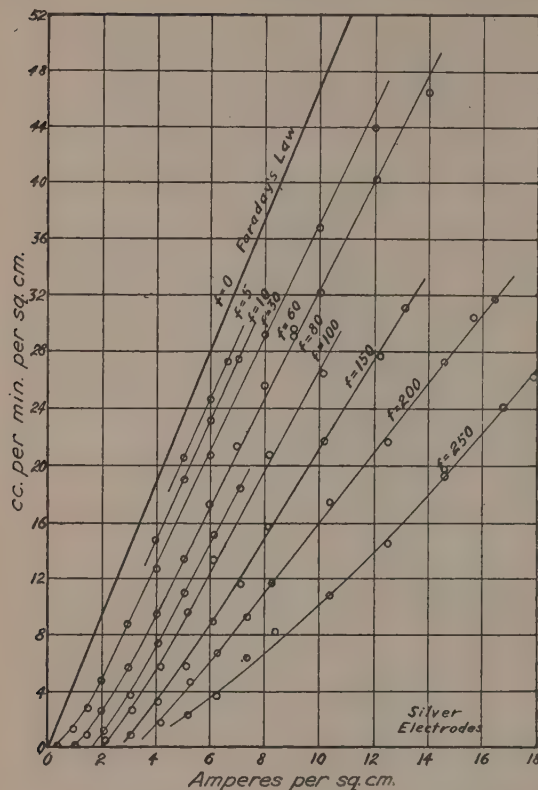


FIG. 8. Relation of current density to rate of generation of electrolytic gases by an alternating current at different frequencies, with silver electrodes.

The departure from the law of A.C. electrolysis observed with platinum was found to exist to an even greater extent with silver electrodes. In no part of the range investigated was an accurate parallelism to Faraday's Law observed. The departure, which was small at low frequencies, increased as the frequency was increased. The results indicate that the electrolytic capacity of silver is not independent of the current density. The experimental results of Van Name and Gräfenberg (2) for 110 cycles, when calculated and plotted as above, lie very close to the observation for 100 cycles shown in Fig. 8.

At current densities of 15 amperes per sq. cm. and above, slight traces of arcing were sometimes observed on the electrodes, but no evidence was obtained of decomposition from this source.

IRON ELECTRODES

Electrodes of iron and steel behaved similarly to the metallic electrodes already described, the curves becoming parallel to the curve for Faraday's Law at relatively low current densities. The increase in the critical current density with increase in frequency was similar to that for copper. The results are not included here because the interpretation in terms of electrolytic capacity is complicated by the complex composition of the iron and steel. For practical purposes in boiler operation, however, the behavior of iron and steel electrodes with changes in frequency may be considered as similar to that of copper.

EFFECT OF THE HISTORY OF THE ELECTRODES

In all experimental work on A.C. electrolysis it has been found that the results obtained depended to a varying extent on the previous history of the electrodes used for the electrolysis. Although consistent results could be

obtained with platinum without difficulty, such was not the case with other metals unless care was taken to see that the electrodes were treated in the same way before actual measurements were made.

IV. Critical Current Density and Electrolytic Capacity

When the frequency is constant, it is seen from equation 3 that the critical current density is dependent on the value of Q_0 . This quantity is here called the "electrolytic capacity", and, as is seen from its origin, is defined as the average storage capacity for electrolytic gases, that is hydrogen and oxygen, on one sq. cm. of metallic electrode surface. It is measured in coulombs. Its value depends on the nature of the electrode surface, temperature, etc., and is the quantity with which alternating current electrolysis is particularly concerned.

ELECTROLYTIC CAPACITY AND THE AREA OF THE QUARTER-WAVE

The departure from Faraday's Law at low current densities and high frequencies for platinum and silver electrodes signifies a lowering of the electrolytic capacity in this range. Decreasing currents and also increasing frequencies cause a decrease in the wave area or the quantity of electricity that has passed before reversal of the current. It is therefore evident that the electrolytic capacity which is the quantity of electrolytic products absorbed, is dependent in some way on the quantity of electrolytic products produced. As the electrolytic capacity takes part in the electrolysis four times in every complete wave, (see Fig. 5), the electrolytic capacity is dependent on the area of the quarter-wave.

Rearranging equation 2 we obtain,

$$Q_0 = \frac{I_1 - \frac{R_1}{4.71}}{4.44f}$$

In place of $\frac{R_1}{4.71}$, we may write I_F , which is the current (measured on an ammeter) required by Faraday's Law to produce gases at the rate R_1 .

Thus changing to millicoulombs we have,

$$Q_0 = \frac{I_1 - I_F}{4.44f} \times 10^3 \quad (5)$$

The value of $I_1 - I_F$ is conveniently obtained by measuring the horizontal distance between any point on the curves and the curve of Faraday's Law. The area of the quarter-wave is given by,

$$q_1 = \frac{I}{4.44f} \times 10^3$$

The values of the electrolytic capacities of platinum and silver at high and low frequencies, plotted against the quarter-wave area, are shown in Fig. 9.

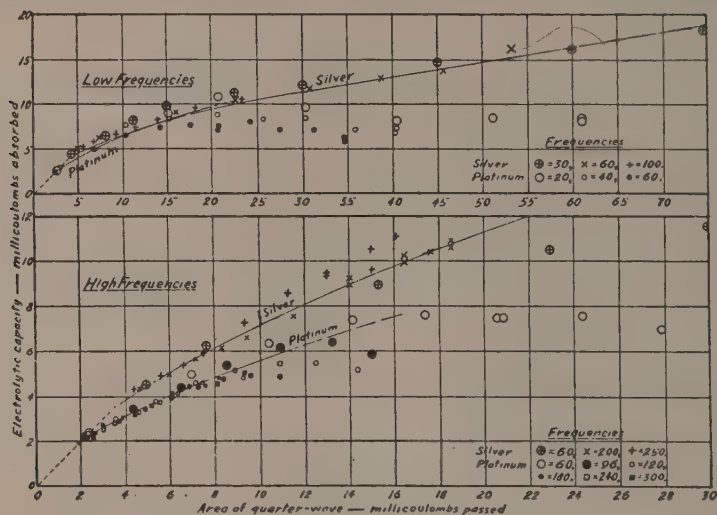


FIG. 9. Relation of absorption to Production of Electrolytic Products, per sq. cm. of electrode surface.

Below the critical point, all of the electrolytic products are absorbed and the electrolytic capacity is therefore equal to the quarter-wave area, as is shown by the dotted line in Fig. 9. Above the critical point, all points obtained from the high frequency curves with platinum electrodes fall about and close to a line which is the average of these points. The electrolytic capacity of platinum approaches a maximum of about 6.5 millicoulombs, after which it generally decreases slightly. This point evidently signifies a saturation of the electrode surface. At lower frequencies (*i.e.*, at longer periodic times) the electrolytic capacity of platinum is slightly higher than at the high frequencies at the same quarter-wave area. The same general form is observed as with the higher frequencies.

Similarly, when all the points on the frequency curves with silver electrodes are resolved into the electrolytic capacity and quarter-wave area that they represent, a single curve is obtained. This is shown for five representative frequencies in Fig. 9. The electrolytic capacity of silver electrodes does not approach a maximum, as with platinum, but continues to increase over the range investigated. From these results it is therefore evident that the quantity of electrolytic products absorbed on a platinum or silver surface during a quarter-wave of alternating current is proportional to the quantity of electricity that has passed during this quarter-wave and independent of current or frequency as such. That is,

$$Q_0 = f(q_1).$$

To obtain the value of this function the logarithms of the values of the electrolytic capacity and of the quarter-wave area were plotted, and in all cases straight line curves were obtained. This signifies that the curves shown in Fig. 9 have the general formula,

$$Q_0 = Aq_1^n, \quad (6)$$

in which A and n are constants representing the absorbing power of the electrode surface. Included in this power are all types of absorption that may take place, such as chemical reaction absorption, adsorption on the surface, or absorption in the surface layer. The values of n and A are obtained from the slope and the intercept on the axis, respectively, of the logarithmic curves.

For platinum the value of n was found to be constant at 0.62 for all frequencies when the value of q_1 was less than 10 millicoulombs. The value of A in this range was found to vary from 1.53 at 20 cycles to 1.34 at 120 cycles, above which it remained constant. The two curves for platinum electrodes shown in Fig. 9 were obtained by using these values of n and A in equation 6. It is seen that there is close agreement between the observed and the theoretical over part of the range. The fact that the electrolytic capacity attains a maximum signifies a saturation of the electrode surface with a constant lowering of the value of n to zero, while the value of A increases until it becomes equal to the electrolytic capacity. (For when $n=0$, $q_1^n=1$ and therefore $Q=A$.) The subsequent lowering of the observed electrolytic capacity is only apparent and is due, without doubt, to the lessening of the active surface of the electrode due to its partial insulation by the large quantity of gas formed. As is seen in the illustration, the value of the maximum increases, as is to be expected, with the periodic time or the time allowed for absorption.

For silver the value of n was found to be constant at low frequencies, but to increase considerably for the higher frequencies. At frequencies of 150 cycles per second and below its value was 0.53, while at 200 it was 0.66 and at 250, 0.77. The value of A was found to be nearly constant at 1.92 for frequencies below 150 but to decrease to 1.55 for 200 cycles and 1.29 for 250 cycles. The curves for silver electrodes shown in Fig. 9 were obtained by using the values of n and A for 150 and 200 cycles in equation 6. Close agreement between the observed and the theoretical was obtained over the entire range and in no case was a maximum or falling off of the electrolytic capacity obtained.

As Q_0 is obtained by difference, the limits of error at high values of q_1 are great, as is seen from the irregularity of the results, and generalisations as to the relation of the absorption constants to frequency cannot be made from these results.

As far as could be determined the value of n for copper was zero over the entire range investigated. The value of A which was therefore equal to the electrolytic capacity, decreased from about 9.0 at 20 cycles to 7.0 at 60 and 90 cycles, above which it could not be accurately determined due to the formation of copper oxide.

RELATION OF ELECTROLYTIC CAPACITY TO FREQUENCY

It is to be expected that if the quantity of electrolytic products, q_1 , be the same, the quantity absorbed will to a certain extent depend on the time allowed for the absorption. It is seen from examination of the platinum curves in Fig. 9, that generally the intercepts of the frequency curves (if drawn) on a vertical line, lie at increasing values of Q_0 as the frequency is decreased. This is also true at low frequencies with silver electrodes, but at higher frequencies exactly the reverse is true. Owing to possible changes in the electrode surface during the time elapsing between the taking of the various frequency curves, the results obtained above were not strictly comparable in this way. Series of experiments over the range of frequency were therefore conducted in which the value of q_1 was maintained constant. That is, the current was increased proportionately to the frequency.

Curves which illustrate the relation with platinum, silver and copper electrodes, are shown in Fig. 10. With platinum, the electrolytic capacity is found to decrease with increasing frequency, as is to be expected, and to reach a minimum at about 120 cycles, beyond which it remains constant.

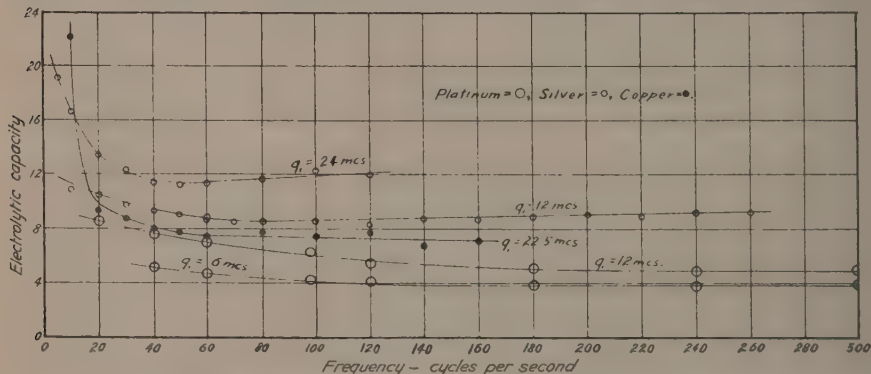


FIG. 10. Relation of the electrolytic capacity to the frequency of the alternations at constant quarter-wave area, q_1 .

With copper electrodes the decrease was more rapid, but the constant minimum was reached at 60 cycles. Silver showed a high electrolytic capacity at low frequencies which in a like manner decreased rapidly to a minimum, but beyond which minimum a decided increase in electrolytic capacity with increasing frequency was invariably observed. Qualitative determinations of the electrolytic capacity at frequencies of one and two cycles per second indicated very high values for the above mentioned metals in this range.

Values of the electrolytic absorption constants, A and n , cannot be obtained from these curves as only their resultant effect is shown. When the values of the electrolytic capacity shown in the figure are plotted against the periodic time in place of the frequency, irregular curves and not straight lines, as might be expected, are obtained. In general, however, it can be stated that the electrolytic capacity increases with increasing periodic time.

THE MECHANISM OF A. C. ELECTROLYSIS

As mentioned above, the existence of the electrolytic capacity of metals has been attributed to absorption by the electrode surface of a quantity of the electrolytic products. This absorption may be of two principal types, chemical absorption, by which we mean the formation of compounds between the metal and one or both of the electrolytic products, or mechanical absorption, such as a solution of the gases in the surface layer.

The similarity between Freundlich's equation for the adsorption isotherm which is:—

$$y = ap^{\frac{1}{n}},$$

(where y is the volume absorbed, p the pressure of the gas and a and $\frac{1}{n}$ are constants) and equation 6 indicates a similarity between the phenomena. It is conceivable that the pressure exerted by the electrolytic products immediately after production may be a function of the total quantity present.

The value of $\frac{1}{n}$, called by Freundlich the "adsorption-exponent", was found to be 0.5 for platinum by Sieverts and Jurisch, (27) which value is remarkably close to the value 0.62 found above. An electrolytic capacity of six millicoulombs as with platinum would require that the metal be capable of absorbing 7.0×10^{-4} cc. of hydrogen, and (in the absence of hydrogen) 3.5×10^{-4} cc. of oxygen per sq. cm. of surface if we assume the individual electrolytic capacities for hydrogen and oxygen to be equal. Graham (10) found a platinum cathode to have absorbed 2.19 times its volume of hydrogen and therefore the above volume could be accounted for if the penetration of the hydrogen was less than 3×10^{-4} cm. below the surface. As compounds of these gases with platinum, if existing, are produced with difficulty, it is altogether probable that the electrolytic capacity of this metal is due to absorption of the gases on the surface or in the surface layer of the electrode.

Experiments at very low frequencies indicated that the mechanism was otherwise with silver and copper electrodes. The following sequence of events was found to take place on the electrodes during every cycle while operating at 3 cycles per second: a short evolution of gas, a uniform but rapid change of the electrode to a deep violet, a short but less vigorous evolution of gas, a uniform but rapid disappearance of the coloration, and so on. By reference to Fig. 5 it will be clear that this sequence indicated: a short evolution of hydrogen which ceases on reversal of the current, a chemical absorption of the oxygen produced to form silver peroxide followed by an evolution of oxygen gas until the second reversal, a chemical absorption of hydrogen to reduce the silver peroxide followed again by an evolution of hydrogen. With the exception that copper oxidized to a black color, the same sequence of events was observed (with this metal) at very low frequencies. This mechanism could be observed to take place up as high as 10 cycles (1) and it is probable

that the electrolytic capacity of silver and copper can be accounted for at all frequencies in this way. In addition to the oxides, hydrides, which are known for both metals, may be formed.

At frequencies of about 150 cycles and above, gas evolution with the above metals as electrodes was accompanied by a loud musical tone of twice the frequency of the alternations. It is evident that the sudden evolution of both hydrogen and oxygen produce a sound wave. The strength of this tone increased with current density.

The chemical nature of the absorption with iron, nickel, and aluminum electrodes has been indicated in a preceding section. The exceedingly low electrolytic capacity found with aluminum was also found to exist with iron under certain conditions. A slightly corroded iron electrode which had been found to have an electrolytic capacity of about 20 millicoulombs, evolved gas after drying in the air for some weeks at a current density of less than 0.05 amperes per sq. cm., which indicated an electrolytic capacity of less than 0.2 millicoulombs. This low electrolytic capacity persisted for some hours after which it regained its normal value. It is probable that the iron oxide becomes passive to reduction by hydrogen when dried.

THE EQUATION OF A.C. ELECTROLYSIS

Converting equation 6 into the units of coulombs in place of millicoulombs, we obtain,

$$Q_0 = \frac{A}{1000^{1-n}} q_1^n$$

This value of Q_0 may now be substituted in the original equation for A.C. electrolysis (equation 1), which gives,

$$R_1 = 4.71 \left(I_1 - \frac{4.44Af}{1000^{1-n}} q_1^n \right).$$

As q_1 , the quarter-wave area, is given by $I_1/4.44f$, the equation for the rate of A.C. electrolysis becomes,

$$R_1 = 4.71 \left(I_1 - A \left(\frac{4.44f}{1000} \right)^{1-n} I_1^n \right) \quad (7)$$

in which the symbols have the same meaning as defined above. It is seen that if n becomes zero the original equation is again produced (A becoming equal to Q_0).

When R_1 becomes zero, that is at the critical point,

$$I_1 = A \left(\frac{4.44f}{1000} \right)^{1-n} I_1^n.$$

The equation of the critical current density is therefore,

$$I_c = A^{\frac{1}{1-n}} \times \frac{4.44f}{1000} \quad (8)$$

Using the values of the constants A and n found above, these equations, 7 and 8, have been found to agree accurately with the experimental results shown in Fig. 6, 7 and 8, for platinum, copper and silver electrodes.

DIRECT DETERMINATION OF ELECTROLYTIC CAPACITY

An apparatus was developed by which an approximate value of Q_0 could be obtained, but by a more direct method than from the critical current density. A pair of electric relay switches were accurately timed to break sharply the connection of the alternating current to the electrodes and connect them to a milliammeter. The movement of the milliammeter was dampened by a high inductance, and the discharge prolonged by resistances. By taking readings of the current at regular intervals until the discharge was complete a close approximation of the total amount of electricity stored on the electrodes at the time of the break in the current could be obtained.

Operating at a current density of 4.1 amp., which was the critical current density for the electrodes used, a large number of discharge readings were taken. They were either positive or negative, and varied from zero to a definite maximum. The average maximum value obtained was 14.7 millicoulombs per sq. cm. of electrode surface for the electrolytic capacity of the metal (iron). Calculating the value of Q_0 from equation 3, it was found in this case to be (frequency 60 cycles) 15.0 millicoulombs per sq. cm. Similar agreement was found in other cases, but due to the short time of discharge the accuracy of the method was limited.

The relation between the magnitude of the discharge and the arc at the contact points on the breaking of the alternating current also gave confirmation of the above theory. Maximum discharges were obtained when the current was broken with a minimum or no arc, and minimum or no discharges were obtained when the arc at the contact points was a maximum. From Fig. 5 it is seen that at the points O, D and T the current is zero, and the arc, if the current is broken at this point, is small. (The phase difference at this voltage was small). At these points the quantity of electrolytic products on the electrodes is a maximum and a maximum discharge is obtained. Similarly at the points C and E the arc is a maximum and the electrodes are in a nearly neutral condition.

These simple and direct experiments showed also that the electrolytic products stored on the electrode exhibit a back electromotive force, and that, whatever the nature of the adsorption which holds them on the electrode surface, it allows these products to regain readily the ionic condition.

ELECTROLYTIC CAPACITY AND NATURE OF ELECTRODE SURFACE

Re-arranging equation 2 we obtain,

$$4.44fQ_0 = I_1 - \frac{R_1}{4.71}$$

But from equation 1 it is seen that $R_1/4.71$ is equal to the current required by Faraday's Law to produce the rate R_1 , which current is called I_F . The equation becomes,

$$Q_0 = \frac{I_1 - I_F}{4.44f} \quad (9)$$

The value of the electrolytic capacity Q_0 can therefore be obtained by dividing the difference between the current density at any rate and the corresponding current required by Faraday's Law for that rate, by 4.44 times the frequency. The value of $I_1 - I_r$ at any particular rate is conveniently obtained by measuring the horizontal distance at this rate between the curve of a metal and the curve of Faraday's Law in Fig. 3 and 4. The frequency in the above experimental work was 60 cycles.

With silver electrodes the value of Q_0 is constant above a current density of 4.0 amp. and is therefore independent of the current density over this range. Its value is 8.6 millicoulombs. Below 4.0 amp. it decreases in value at first slowly and then more rapidly, until at the critical point its value is 6.0 millicoulombs. A greater divergence is seen with platinum electrodes. The value of Q_0 , constant at 6.7 millicoulombs above 4.0 amp., decreases to 2.6 millicoulombs at the critical point of 0.7 amp.

This variation of the electrolytic capacity with current density near the critical point may be accounted for by the lower voltage in this range, and consequently a lesser "driving force" to assist in the absorption of the electrolytic products into the surface layer of the electrode. This effect, appreciable in the case of platinum, is small with silver electrodes and is practically non-existent with the other metals used. The elevation of the current density above the critical point of platinum, which means a super-saturation of the electrode surface over its normal capacity, is accompanied by a visible change in the surface coating. The surface coating is probably finely divided platinum possessing a greater surface and a greater storing power than the normal surface.

Copper, being a readily oxidizable metal, and copper oxide a readily reducible substance, it is to be expected that a copper oxide-coated copper electrode would give a very high electrolytic capacity, and a large elevation of the critical current density. Such is actually found to be the case as shown by the part "a b" of curve B in Fig. 4. With the bright copper surface the electrolytic capacity is a constant, entirely independent of the current density. Its value is given in Table III. The curve for copper was drawn with a straight edge parallel to the curve for Faraday's law and touches all points.

Bright metallic surfaces, free from oxides, as with silver, platinum, and copper, could not be maintained for experimental determination of the electrolytic capacity of steel, soft iron and nickel electrodes. The electrolytic capacity was therefore greater than with the metallic surfaces. Apparently the thin oxide coating on these metals was of uniform thickness, as they follow the law of A. C. electrolysis.

TABLE III

THE CRITICAL CURRENT DENSITY AND ELECTROLYTIC CAPACITY OF VARIOUS METALS*

Metal	Current density or range	Critical current density amp. per sq. cm.	Electrolytic capacity millicoulombs per sq. cm.
Silver	4.0-10.0	1.6	8.6
Silver	1.6	1.6	6.0
Platinum	4.0-6.4	0.7	6.7
Platinum	0.7	0.7	2.6
Copper	1.9-10.5	1.9	7.1
Copper (oxide coated)	10.0	10.0	37.6
Steel, 0° C.	4.5	—	10.9
Steel, 30° C.	4.5-10.0	4.5	16.9
Steel, 80° C.	4.5	—	22.6
Steel (corroded)	8.0	8.0	30.1
Steel (corroded)	14.0	8.0	35.3
Soft iron	3.8-10.0	3.8	14.3
Nickel	9.0	4.6	19.6
Aluminum (0.5N. H ₂ SO ₄)	0.01	<0.01	<0.037

*Measured in 0.5 N. sodium hydroxide solution at 30° C., and with a frequency of 60 cycles.

At current densities above 6.0 amp. the values of Q_0 for iron and steel were constant, as seen from the constant difference between the curves B and A and the curve of Faraday's law in Fig. 3. The slight departures near the critical point are likely due to a combination of the effect of low voltages and an elevation of the critical current density.

The relation of electrolytic capacity to the nature of the surface is strikingly shown by the curve for heavily corroded steel in Fig. 3. The critical current density is practically double that of the normal steel. A further increase in the electrolytic capacity is observed at high current densities, due probably to the increased "driving force" of the higher voltage.

The electrolytic capacity of nickel electrodes becomes constant only at high current densities, changes in the surface coating probably accounting for the abnormal curve. Aluminum has a very low electrolytic capacity, if any, as might be expected from its chemical properties, aluminum oxide being non-reducible by hydrogen. A similar result was obtained by A. Günther-Schulze (12). Aluminum on the other hand gives a very high electrostatic capacity (36) and is used for condensers.

THE EFFECT OF FREQUENCY AND TEMPERATURE

Experimental work by Maneuvrier and Chappuis (2) and by Marsh (2) has shown that the rate of electrolysis decreases with increase in frequency. Malagoli (2) considers the relation a straight line function with a negative slope. From equation 2, which is,

$$R_1 = 4.71 (I_1 - 4.44fQ_0) \quad (2)$$

it is seen that if I_1 and Q_0 are constant the rate is directly related to the frequency in a negative direction. If the frequency is zero, that is a direct current,

the rate becomes equal to Faraday's equivalent. It is doubtful that Q_0 is independent of the time of charging the electrode. Increasing the periodic time would allow the electrolytic products to penetrate the electrode to a greater extent, thereby increasing the electrolytic capacity. Preliminary experiments indicate that this is probably the case.

Experimental evidence obtained by the author has shown that the electrolytic capacity with some metals varies greatly with temperature, and with others only slightly. The electrolytic capacity of steel electrodes increases rapidly as the temperature is raised from 0° to about 80° . An increase of from 10.9 millicoulombs at 0° C. to 22.6 millicoulombs at 80° C. is found on applying equation 3 to the curve of critical current density plotted against temperature, as given in a previous paper (29).

A decrease in the capacity was observed concurrently with the production of steam on the electrodes, and is probably due to the washing effect of the bubbles of steam. A much smaller variation was obtained with platinum. For example, at a current density of 3.0 amp. the electrolytic capacity was found to decrease from 6.4 millicoulombs per sq. cm. at 0° C. to 6.0 at 50° C. increasing again to 7.1 at 85° C. and decreasing at the boiling point.

ELECTROMOTIVE FORCE CONSIDERATIONS

As is generally understood, on the first passage of current a Helmholtz double layer is produced which exerts a back E. M. F., and an equal and opposite force, which is the theoretical decomposition voltage, must be applied to overcome this. A further E. M. F. to overcome overvoltage and the resistance of the electrolyte, must be applied to cause the current to flow. Although a large amount of work has been done relating voltage to current density and in connection with overvoltage in general, the relation of voltage to the quantity of electrolytic products on the electrodes, or to the coulombs that have passed has not been definitely established.

Kohlrausch (20) assumes that the polarization voltage is directly proportional to the quantity of electricity that has passed, and gives experimental proof to show that this is true up to ten microcoulombs per sq. cm. Despite this limited range Mengarini (2) considers it applicable over a wide range, and even in recent times Lattey (21) makes use of it without question as to its validity. By an original and direct method Griffiths and Heys (11) found that this relation holds up to three microcoulombs per sq. cm. with platinum electrodes, but above this the direct proportionality no longer exists.

Somewhat similar results were obtained through a different method by Clark (6), who found an approximate linear relation up to about 2.4 millicoulombs per sq. cm., but he considers it to be more of an exponential than a linear function. In the course of an investigation into the effect of superimposing an A.C. on a D.C., Jones (17) obtained the relation between coulombs and overvoltage (what we refer to as decomposition voltage) for lead electrodes. He found that the voltage rose regularly with the quantity of electricity, to a point where the curve flattened out.

From the above experimental work it is apparent that electrodes act as condensers at low voltages.

DETERMINATION OF BACK ELECTROMOTIVE FORCE

Experiments were carried out to determine the relation existing between voltage and the quantity of electricity passed, with the purpose of connecting the results to the theory of alternating current electrolysis. A potentiometer was used to cause low currents to pass through two platinum electrodes immersed in sodium hydroxide solution. The electrodes exposed a known area of surface and were protected from stray currents. The current was measured by a calibrated galvanometer and the potentiometer readings corrected for the fall, due to the current passing and the resistance of the circuit. The potentiometer was varied to maintain a constant current through the electrodes, and voltage readings were taken at intervals timed by a stop-watch. The electrodes were reversed between each series.

Sufficient evidence has been obtained to show that, at a direct current density of 100 microamperes per sq. cm. and above, the voltage rises rapidly until about one millicoulomb per sq. cm. has passed. Beyond this the voltage increases but little, no matter how long the current has passed. This is shown in Fig. 11.

No visible evolution of gas was obtained, which is accounted for by the solution of the small quantities of gas in the electrolyte.

At current densities of about one microampere the maximum voltage was less than half the voltage obtained at 100 microamperes.

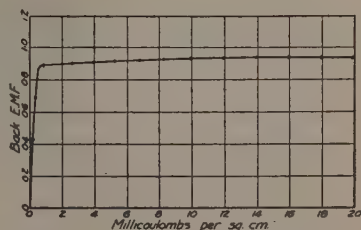


FIG. 11. Relation of back E.M.F. to the quantity of electricity passed through one sq. cm. of electrode surface.

POLARIZATION CAPACITY

It may therefore be considered that the electrodes act as "leaky condensers" up to the theoretical decomposition voltage of the electrolyte. This similarity was first pointed out by Varley (34) and by Kohlrausch (20). Above this voltage, decomposition takes place and the electrode becomes polarized, an increase in voltage or overvoltage (25) being required to cause the current to flow. The electrostatic capacity exhibited by electrodes below the decomposition voltage has been termed by Kohlrausch the "polarization capacity," although up to the decomposition voltage, polarization, as we now understand it, probably does not take place.

A large amount of experimental work (21) was performed to measure this so-called "polarization capacity," but with conflicting results. In more recent times Vaillant (33) and Sorrel (31) measured the polarization capacity in relation to current density. Clark (6) and Griffiths and Heys (11) measured

the capacity and related it to the charge put into the electrode. The relation of this capacity to frequency has been investigated by Haworth (13), Merritt (23), Jolliffe (16), Wolff (35), Banerji (3), Smith and Moss (30), and a number of others (21), but as yet no definite generalizations have been obtained from their results.

The value of this capacity has been found to be of the order of 10 microfarads per sq. cm. for platinum electrodes. A value of about 12,000 ohms per sq. cm. for the resistance of the "leaky condenser" can be obtained from the leakage curve, given by Griffiths and Heys (11), for platinum in sulphuric acid. Preliminary experiments conducted in this laboratory indicate that the resistance for platinum electrodes in sodium hydroxide solution is of the order of 25,000 ohms per sq. cm.

This capacity effect is credited by a number of authors (36, 13), to the formation of a gaseous film between the electrode and the electrolyte, but this conception is hardly tenable below the decomposition voltage. Furthermore, the mechanism by which it is built up, while still allowing the current to pass, is difficult to conceive. If the equation,

$$C = \frac{KA}{4\pi d} \times \frac{1}{9 \times 10^5} \text{ mfd} \quad (10)$$

for the capacity of a parallel plate condenser (K = dielectric constant, A = area, d = thickness of dielectric) holds down to atomic dimensions, the thickness of a gaseous layer, to produce such a capacity may be obtained.

To give a capacity of 10 mfd, a thickness calculated from equation 10 of approximately 10^{-8} cm. would be required, which is of atomic dimensions. The spacial separation of molecules of a gas is of the order of 10^{-7} cm. and as a layer ten molecules thick would be hardly sufficient to separate the walls of the condenser, the minimum thickness of the gaseous film would have to be of the order of 10^{-5} or 10^{-6} cm., that is 100 to 1,000 times as great. We must conclude therefore that the condenser effect is not due to a gaseous film, as such, or that the equation for the capacity of a condenser shows very wide variation at small thicknesses.

If, as with Clark (6) and Banerji (3), we consider the effect as due to the Helmholtz double layer, a better agreement with the thickness of the dielectric is obtained. If a low potential is applied to the electrode it will attract the oppositely charged ions to itself, but will not be sufficient to cause the electron to cross the intervening space, whatever its nature may be. The requirements of a condenser are fulfilled.

If the dielectric is compressible the capacity of the condenser will increase slightly with the voltage. Such was actually found to be the case with platinum by Griffiths and Heys (11) and with a number of other metals by Clark (6). As one part of the double layer is composed of ponderable ions, an increase in frequency would not allow the ions to approach the electrode as closely and a decrease in the capacity would be obtained. Such is found to be the case by the experimenters referred to previously.

The layers of the condenser are not rigid but are composed of rapidly vibrating particles. It is conceivable, therefore, that two oppositely charged particles might come into sufficient contact to allow an electron to pass below the decomposition voltage. This would account for the leak observed with electrolytic condensers.

ELECTROLYTIC CAPACITY AND POLARIZATION CAPACITY

At the theoretical decomposition voltage the electrostatic condenser breaks down and electrolytic products are produced on the electrode surface. These products are not immediately removed from the surface, but are stored in some manner in the surface layer. Their presence causes an increased resistance or a polarization of the electrode surface. Gas will be liberated when the storage capacity of the electrode surface is satisfied. *The average of the quantities of electricity per sq. cm. which must pass after the theoretical decomposition voltage is reached, before electrolytic gaseous products are liberated from each of the two electrodes* we have called the "electrolytic capacity" of the metal as determined by this research. The term "polarization capacity" we have limited to the range below the decomposition voltage and is an electrostatic capacity. Jolliffe (16) used these terms as if identical, but a distinction has been made in this research.

The measurement of electrolytic capacity by the rate-current density curves or the direct method given above necessarily includes the effect of the polarization capacity, and it was for this reason that the above experiments were performed to find the relative effects of the two capacities. Let us consider a platinum electrode which exhibits a polarization capacity of ten microfarads, which is the average value, in an electrolyte with a theoretical decomposition voltage of one volt.

The quantity of electricity required to bring the electrode to this voltage would be ten microcoulombs. The electrolytic capacity of platinum determined above was about five millicoulombs or 500 times as great. The effect of polarization capacity on the electrolytic capacity in alternating current electrolysis of water is therefore negligible under the conditions of current density, frequency, etc., given above.

V. Phase Difference

The curve of back electromotive force (Fig. 11) may now be applied to the sine wave of the alternating current. A current starting at the point A (Fig. 12) and varying as the sine of the angle will follow the path ABC. This current is passing through two electrodes and an electrolyte. The voltage required to overcome the ohmic resistance of the electrolyte, known as the "IR drop", is shown by the curve DEF.

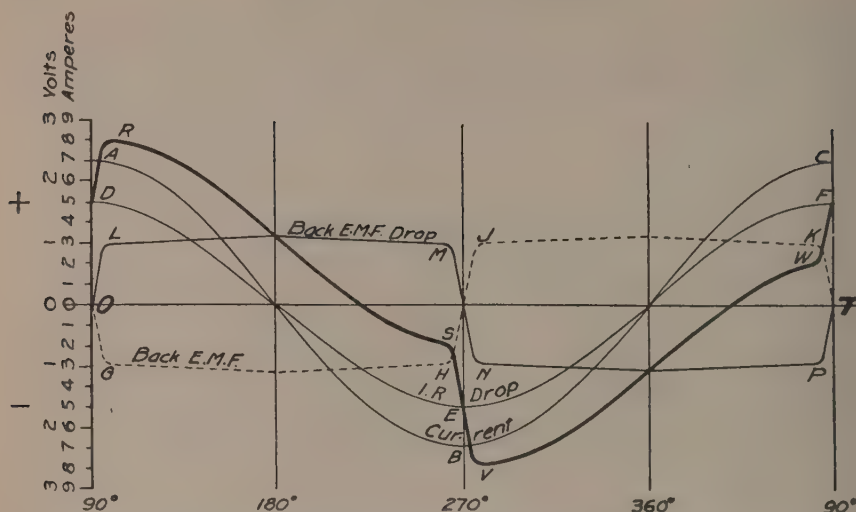


FIG. 12. Diagrammatic representation of the phase difference and distortion of wave form produced by the back E.M.F. of an electrolytic cell.

On the passage of current an electromotive force opposing the current will be set up immediately, and will increase at a rate depending on the current and the polarization capacity of the electrode, until the theoretical decomposition voltage of the electrolyte has been reached. This is represented by the point G and the dotted line. On further passage of the current the voltage will rise only slightly, irrespective of evolution of gas. This overvoltage will increase with current density.

On reversing the current the back E.M.F. will fall only slightly, until the hydrogen produced has neutralized the oxygen adsorbed on one electrode and *vice versa* on the other. If we assume that the individual electrolytic capacities of the metal for hydrogen and oxygen are equal, and operate at the critical current density, the back E.M.F. will drop suddenly at the point H to zero, and immediately set itself up in the opposite direction, until the same decomposition voltage has been reached. It will then proceed along the path JK until the hydrogen on one electrode and the oxygen on the other have been completely neutralized and fall to zero at the point T.

If the individual electrolytic capacities of the metal for hydrogen and oxygen are not equal, the reversal of the single electrode potential at each electrode will take place at different moments. The drop from H to J in Fig. 12 will take place in two parts at the instants of these reversals, the first drop taking place before point H is reached. Operating above the critical current density the curve of the back E.M.F. will not change its shape, but will be displaced to the left, depending on the distance of the current density from the critical point. Operating below the critical point, the value of the electrolytic capacity

will not be fully satisfied, but the curve will be the same as in the figure. The first two of these variations from the above conditions will thus cause the point of maximum back E.M.F. to be displaced to the left.

An equal and opposite E. M. F. of the same value as the back E. M. F. will then have to be impressed to maintain the current flowing. This E. M. F. is shown in the figure by the curve OLMNPT. Combining this curve with the curve of the "IR drop" DEF, the resultant voltage curve DRSVWF, shown by the heavy line, is obtained.

As seen in Fig. 12 there is a difference between the phase of the current and of the voltage, the current leads the voltage as in a condenser circuit. This phase difference has been discussed by Cooper (7). The theoretical considerations of Mengarini led to a phase difference, in which the voltage led the current, but this is not in accordance with observation. Confirmation of the above theory is found in the alternating current and voltage curves obtained by Hopkinson, Wilson and Lydall (2) which show a phase difference as high as 72° C. with the current leading the voltage. Their curves for the voltage do not follow the sine law and show considerable irregularity. In some cases indications of the distortion shown in Fig. 12 are seen.

The extent of this phase difference and the distortion of the wave form will decrease as the current and the resistance are increased. For the same current and resistance this difference will vary for different metals, and vary with their critical current density, and the individual electrolytic capacities of the electrode for hydrogen and oxygen.

An oscillograph was employed to determine experimentally the phase relationships of current and voltage. Determinations were carried out with both platinum and copper electrodes using potassium hydroxide as electrolyte. It was expected that the oscillographs obtained would show a difference in the phase of the current and voltage, the current leading the voltage. The extent of the phase difference and the distortion of the wave form should decrease as the current and resistance are increased. For the same current and resistance the phase difference should vary for different metals with the critical current density of these metals and the individual electrolytic capacities of the electrode for hydrogen and oxygen.

APPARATUS

Two platinum electrodes were made by sealing circular platinum discs of diameter 2.2 cm. on one end of each of two short sections of thick-walled glass tubing of the same diameter, this end being previously ground to a smooth surface perpendicular to the walls of the tubes. Electrical connection was made with glass-sealed platinum wires and mercury. The electrodes, filled and sealed with wax, were inserted in a glass tube of diameter only slightly larger which kept them close together and parallel. The electrolyte was 5.0 N. KOH (which is near the point of maximum conductivity) and was kept circulating

rapidly through the electrode chamber. The electrodes were made almost the size of the electrode chamber to obtain as far as possible the condition of uniform current density while still allowing the electrolyte to flow.

Copper electrodes were made from short sections of copper rod with an all copper connection. All but the polished faces were insulated with rubber tubing and cement. Considerable difficulty was encountered in obtaining a cement to withstand the electrolyte, but DeKhotinsky cement or Duco varnish when baked for some time were found to last sufficiently for a series of experiments.

The oscillograph was of the standard type and wired to suit the experiments. All measurements were taken on one vibrator, a series of switches being arranged whereby the zero current, voltage and standard D.C. voltage waves could be impressed in succession. The current was varied by a series of rheostats down to a current of 0.2 amperes below which it could not be read accurately on an ammeter. The lower range was obtained by standard resistances and voltage readings.

Considerable difficulty was at first encountered in removing the effects of mutual and self-induction; this was finally overcome by a careful rearrangement of wiring and assembly of electrical apparatus, the absence of these effects being shown by means of blank tests. To prevent changes in the sine form of the current wave by distortion of the voltage wave a voltage of about 90 was used and lowered by low inductive resistances.

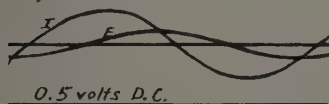
In place of the rotating film, records were usually taken by placing a fast bromide paper, by means of a special adapter, on the mica screen used for visual observation. The time factor is introduced on this screen by means of a synchronously vibrating mirror. On this account, possible errors, as yet not fully determined, may be introduced in the phase difference. On the other hand the rapidity with which observations could be made by this method compared to the usual rotating film method, made it possible to take a larger number of readings, and to overcome the difficulty arising from changes found to take place in the electrode surface on long standing.

PLATINUM ELECTRODES

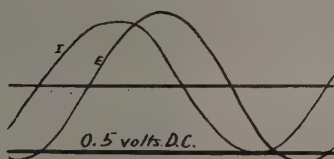
With an alternating current at a frequency of 60 cycles three series of photographic records were taken over a wide range of current densities with platinum electrodes at different distances apart. Sample records taken from one of these series are shown in Plate I. The distance between the electrodes was 0.015 cm. and the temperature 20° C. The current, current density, maximum voltage and phase angle are marked on each record. The maximum voltage is obtained by comparison with the standard D.C. voltage.

At low currents no distortion is visible, as is seen in records No. 2 and No. 6, but at current densities near the critical point considerable distortion takes place. The oscillograph records in this range show two breaks in the voltage

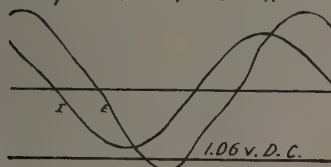
19/3/27, #2

 $I = 0.024 \text{ Amps.}$, $E_m = 0.11 \text{ v.}$
 $I_f = 0.0063 \text{ "}$, $\theta = 68^\circ$.


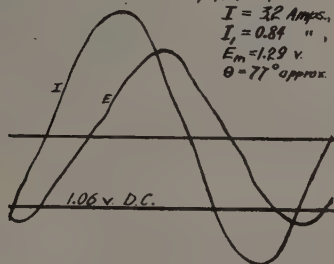
19/3/27, #6

 $I = 0.12 \text{ Amps.}$, $E_m = 0.55 \text{ v.}$
 $I_f = 0.032 \text{ "}$, $\theta = 62^\circ$.


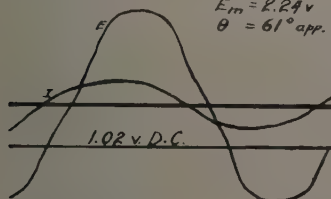
19/3/27 #10.

 $I = 1.60 \text{ Amps.}$, $E_m = 1.21 \text{ v}$
 $I_f = 0.42 \text{ "}$, $\theta = 75^\circ \text{ approx.}$


19/3/27 #12.

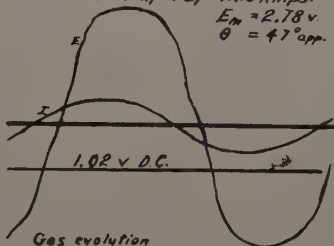
 $I = 3.2 \text{ Amps.}$
 $I_f = 0.84 \text{ "}$,
 $E_m = 1.29 \text{ v.}$
 $\theta = 77^\circ \text{ approx.}$


19/3/27, #14

 $I = 3.2 \text{ Amps.}$, $I_f = 0.84 \text{ Amps.}$
 $E_m = 2.24 \text{ v}$
 $\theta = 61^\circ \text{ app.}$


Gas evolution

19/3/27, #17

 $I = 4.8 \text{ Amps.}$, $I_f = 1.26 \text{ Amps.}$
 $E_m = 2.78 \text{ v.}$
 $\theta = 47^\circ \text{ app.}$


Gas evolution

curve, one when the current is a maximum and one at the reversal of the current. This first break occurs as was predicted. Typical examples of such distortions are shown in records No. 10 and No. 12, Plate I.

Above the critical point a greater distortion of the voltage wave takes place, and as in the case of No. 17, approaches a rectangular shape.

COPPER ELECTRODES

In a similar manner and under the same conditions two series of photographic oscillograph records were taken with copper electrodes. Examples of one series are shown on Plate II. The distance between the electrodes was 0.12 cm. Distortion of the wave form of the voltage appears at a current density of 0.1 amperes and above. Two distinct breaks in the curve occur at about 60° C. and 120° C. in each current half-wave.

MAXIMUM VOLTAGE

When the maximum of the voltage wave produced by an A.C. in the above electrolytic cells was compared with the quarter-wave area or the current density and plotted against quantity of electricity passed, a curve was obtained quite similar to that given for the back E. M. F. (See Fig. 12). The voltage curve for both the platinum and the copper rose rapidly at first and then flattened out to a straight line with a slope *which gives the same resistance for the cell as that calculated from the dimensions of the cell and the conductivity of the electrolyte*. This indicates that an electrolytic cell acts as a condenser up to a point near but below the decomposition voltage; above this point the resistance of the "leak" of the condenser decreases and eventually completely breaks down, leaving a constant back E.M.F. and the resistance of the electrolyte to oppose the current. Assuming the resistance to be infinite and the sine of the phase angle equal to 1, the capacity of the condenser for the platinum electrodes was found to be 225 microfarads per sq. cm. and for the copper electrodes 150 microfarads per sq. cm. These values are probably a little high because of the decrease in the maximum voltage determined by the oscillograph and the corresponding increase in the capacity values. A variation of the distance between the electrodes did not affect the nature of the results.

Comparing the wave angle with the quarter-wave area (current density) it was found that with platinum electrodes below the critical current density the phase angle was constant, except at very low currents, while above this point it decreased rapidly with an increase in current. This behavior was in accordance with the theoretical considerations given in a previous paragraph. Copper electrodes behaved somewhat differently, the phase angle rising to a maximum but decreasing at higher current densities. This irregularity at lower current densities may be due to variations on the electrode surface.

ANALYSIS OF CURVES

Although the oscillographs obtained cannot be considered as exactly tracing the relationships of electrolytic capacity effects to current density, yet the analysis of some of the curves was thought to be of some value. The curve obtained with copper electrodes shown in record No. 15, Plate II, was projected by means of an enlarging camera on a graph paper screen and the measured voltage tabulated at 5° intervals. The corresponding IR drop was calculated for each 5° interval, on the assumption that a sine wave was produced, by means of the resistance estimated from the dimensions of the cell. The difference between the IR drop and the voltage recorded was the back E.M.F. of the cell. The resultant curve was found to be 90° behind the curve of the current wave, and was characterized by two distinct breaks in the wave form. The position of the breaks indicated that the individual electrolytic capacities of copper for hydrogen and oxygen were different and that the reversal of the single electrode potential of each electrode took place at different moments.

Until a true wave of the back E.M.F. is obtained, quantitative interpretation of the oscillographs cannot be made. Compensation for the IR drop might eliminate one of the uncertainties. It was therefore made by superimposing the wave representing this drop upon the voltage wave; the superimposed wave was obtained by the use of specially designed, variably coupled transformers. Qualitatively the oscillographs, examples of which are given in Plates I and II, support the theoretical considerations arising from the work on A. C. electrolysis.

VI. Decomposition of Water by High Voltage Arcing

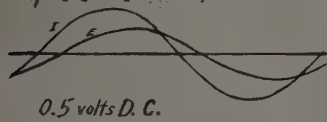
Electric steam generators operate at high voltages producing arcing upon the electrodes. Kaelin and Matheson (18) found in the operation of miniature electric boilers at high voltages that electrolytic gases in excess of the volume produced by the decomposition of the water were formed when arcing occurred upon the electrodes. Water has been found by Loeb to be decomposed by the electric arc but no quantitative investigation appears to have been made into the decomposition of water by the arc under water.

The investigations described so far in this paper had been conducted at relatively low voltages and although arcing had been observed, no particular increase in the quantity of gas had been obtained above that required by the law of A. C. electrolysis. However, since electric steam generators operate up to 6,600 volts or higher it was deemed desirable to extend the investigation to higher voltages and quantitative measurements of the rate of decomposition of water by arcing were made up to 4,200 volts.

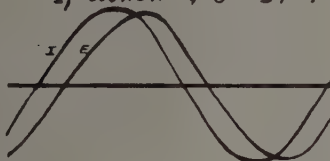
APPARATUS

The apparatus was similar in construction to that used previously and shown in Fig. 1. The electrodes of piano wire steel were placed 4 cm. apart on a pair of rubber stoppers suitably mounted on glass rods. Connection to the electrodes was made through thick-walled glass tubing. The whole was

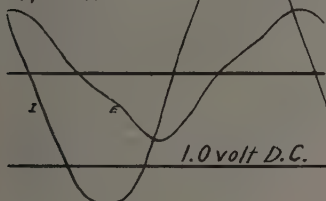
9/4/27 #2

 $I = 0.0269 \text{ Amps.}, E_m = 0.179 \text{ v.}$
 $I_1 = 0.0068 \text{ "}, \theta = 30^\circ$


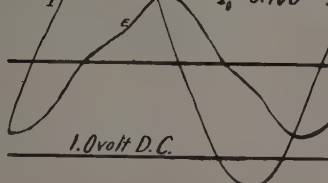
9/4/27 #5

 $I = 0.1 \text{ Amps.}, E_m = 0.52 \text{ v.}$
 $I_1 = 0.0252 \text{ "}, \theta = 31^\circ$


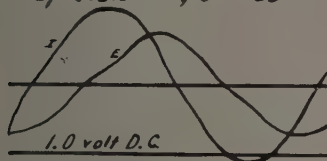
9/4/27 #8

 $E_m = 0.69 \text{ v.}, \theta = 57^\circ$
 $I = 0.80 \text{ Amps.}$
 $I_1 = 0.203 \text{ "}$


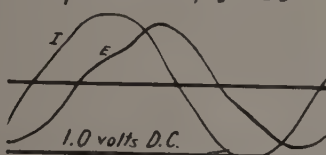
9/4/27 #10

 $E_m = 0.74 \text{ v.}, \theta = 60^\circ$
 $I = 1.60 \text{ Amps.}$
 $I_1 = 0.406 \text{ "}$


9/4/27 #12

 $I = 2.40 \text{ Amps.}, E_m = 0.76 \text{ v.}$
 $I_1 = 0.610 \text{ "}, \theta = 63^\circ$


9/4/27 #15

 $I = 4.80 \text{ Amps.}, E_m = 0.88 \text{ v.}$
 $I_1 = 1.219 \text{ "}, \theta = 53^\circ$


contained in a four-litre Pyrex beaker mounted on an auxiliary electric plate heater. Steam that was formed collected in a large funnel, passed up to the top of a condenser, and the condensate returned to the boiler. The residual gases collected in a bulb on the top, from which they were drawn to a water cooled measuring tube. The residual gases were analysed for electrolytic gases (two parts of hydrogen to one of oxygen) by explosion in a eudiometer tube, and for excess hydrogen by second explosion with a known quantity of air.

The power was obtained from a 60-cycle 110-220 volt source and was connected by means of controlling switches through a bank of low resistances for delicate adjustment and an ammeter bank, to the transformers. The two transformers used, either singly or in various combinations of the pair, gave a voltage range of 345 to 4200 volts. The current through the boiler was measured by an ammeter in the secondary circuit, or, as was occasionally necessary when below the range of the ammeter, by calculations from an empirical relation of the primary and secondary currents. The voltage was stepped down to a convenient voltage for measurement by standard potential transformers. To prevent stray currents travelling through the layer of condensed steam, all high voltage connectors were rubber insulated and enclosed in glass and sufficient safety precautions were included in the design to exclude the possibility of accident.

Conductivity water of a high degree of purity was used as a base for the electrolyte and a known quantity of sodium hydroxide added as desired to increase the conductivity. The concentration of the resulting electrolyte could be controlled and its value calculated.

RATE OF DECOMPOSITION OF WATER BY HIGH VOLTAGE ARCING

Operating with 2100 volts across the two electrodes, whose diameter was 0.124 cm. and length 2.56 cm. making an area of exposed surface of 1.0 sq. cm. the rate of formation of residual gases on the condensation of the steam was determined at intervals of increasing current. The resistance of the electrolyte was decreased by adding known quantities of 0.1 N sodium hydroxide and the electrolyte was maintained continuously boiling by means of the auxiliary heater. The residual gas over a definite interval of time for each current was analysed for hydrogen and oxygen.

At low currents no arcing was observed, and the rate of formation of residual gas was very low, which gas on analysis was not found to contain hydrogen. On increasing the current, traces of hydrogen were produced at the rate of less than 0.01 cc. per minute. At a current of 0.31 amperes (and therefore in this case the same current density) arcing occurred, and the products of decomposed water appeared at a definite rate. On increasing the current still further, the arcing increased and the rate of production of hydrogen and oxygen increased very rapidly. The rate in cc. per minute at S.T.P. of hydrogen and oxygen is plotted against the current in Fig. 13. The analysis showed in all cases a

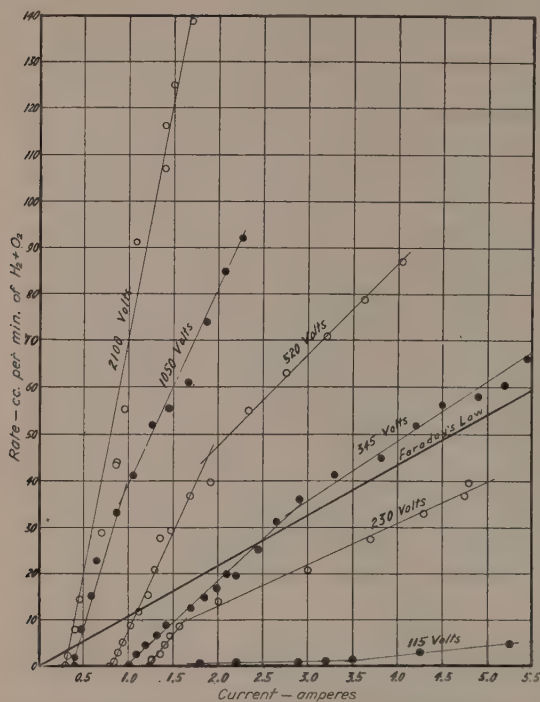


FIG. 13. Rate of decomposition of water by high voltage arcing at various voltages.

arcing, which increased rapidly with increasing current.

At voltages of 345 and 230 the production of hydrogen was observed before arcing commenced, in a quantity indicating a rate of about 0.5 cc. per min. of electrolytic gas. This is undoubtedly due to electrolytic decomposition by the A. C. as already described. The rate increased very slightly with increasing current until arcing commenced after which point the rate increased rapidly as is shown in the figure. The rate curve at 230 volts is very nearly parallel to the curve of Faraday's Law. At these voltages the current was above the critical current density over the upper part of the curve and gas therefore was being produced by both A. C. electrolysis and by decomposition in the electric arc.

With 115 volts between the electrodes arcing commenced at a current of about 2.9 amperes, below which the rate of production of electrolytic gas was 0.73 cc., and above which it increased but slightly with increase of current and arcing. The electrodes remained a deep brown color throughout and the rate of gas evolution was very low even though the critical current density was greatly exceeded. This elevation of the critical point (29) was frequently observed at higher temperatures, but at very high current densities (e.g., 13

quantity of hydrogen of more than twice the oxygen, the average analysis showing 65% hydrogen and 30% oxygen, the remainder probably being nitrogen. The electrodes at low currents were coated brown with oxide which disappeared leaving a dull metallic lustre when the arcing became very vigorous.

In a similar manner and under the same conditions the rate of decomposition of water with increasing current at 1050 volts and at 520 volts was determined, the results of which are shown in Fig. 13. Traces of hydrogen were observed before arcing commenced, but a regular rate of production appeared only with

amperes per sq. cm.) the oxide coating was removed, the rate of gas formation rose rapidly, and finally followed a curve approximately parallel to but below Faraday's Law, in accordance with the law of A. C. electrolysis. Although the arcing at 115 volts was at times considerable, the rate of gas formation was never greater than could be expected from A. C. electrolysis.

In the 1050, 520, 345 and 230-volt curves, a decided change in slope occurs. Owing to the large errors in the readings a continuous curve could not be correctly drawn, therefore the relation is shown by two straight lines. The principal error was in the reading of the current, which varied greatly, but in addition at high rates of gas evolution part of the gas was sometimes lost due to overloading of the steam condensing system.

Attempts were made to conduct a series of experiments at 4200 volts but the design of the apparatus was not such as could cope with the steam produced, nor prevent arcing directly across from one electrode to the other even when spaced 4 cm. apart. Observations made, however, indicated that the curve lies to the left of the 2100 volt curve shown in Fig. 13.

The voltages recorded represent the potentials existing between the electrodes, but the primary factor in high voltage arcing is undoubtedly the *potential gradient in the neighborhood* of the electrodes. This potential gradient will depend on the distance between the electrodes, their diameter, shape of electrode chamber, etc.

The complete independence of the rate of decomposition of water at high voltages from Faraday's law and the law of A. C. electrolysis, is one of the outstanding observations established from our experiments. The critical point above which electrolytic gases are produced at high voltages is the point at which arcing commences. It will be observed that the slope of the curves for the rate of production of electrolytic gases increases regularly with the voltage, the slope of the upper part varying directly with the voltage. This relation of gas production to voltage will be discussed in a succeeding paragraph.

CHARACTERISTICS OF THE ARC

On increasing the current to the arcing point arcs of momentary duration made their appearance at intervals on any part of the surface of the electrode. It was usually observed that boiling was more vigorous on one electrode than the other, depending probably on the direction of flow of the electrolyte. In some cases the electrolyte would boil vigorously on one electrode, while at the same time no evidence of steam formation would be visible on the other. Similarly, arcing would often take place on the electrode that was producing the steam and alternate between the two electrodes with steam production. This is to be expected from the increase of resistance in the neighborhood of the electrodes with production of steam.

At high currents the arcing appeared to be a continuous flame emanating from all points on the electrode. At all times the arc extended radially into the electrolyte.

Arcing was accompanied by a vigorous, audible vibration, but the commencement of the sound was not coincident with but preceded the commencement of arcing. With electrodes close together and at high voltages arcing from one electrode across to the other was of frequent occurrence. For example, with the electrodes described above, spaced four cm. apart, the electrolyte was found to break down and thus establish an arc from one electrode to the other under a difference of potential of 4200 volts with a current of 1.45 amperes.

ENERGY RELATIONS

An interesting relationship is brought out by plotting the rates at the various voltages shown in Fig. 13 against the electrical energy used up per minute by the electric boiler, as is done in Fig. 14. All of the points of the curves at 1050, 520, 345 and 230, and the points in the upper part of the curve at 2100 volts, lie about two straight lines which are drawn as composite lines. Our results therefore indicate that for a given pair of electrodes *the amount of the gaseous products of decomposition of water at high voltages is directly proportional to the quantities of electrical energy used up.* The curve at 2100 volts in its

lower part does not conform with this relation. Numerous experiments were carried out at this voltage, and this departure was confirmed by their results. Similarly the 4200-volt curve in which the currents were very low, lay below the curves for the lower voltages. The significance of this will be discussed later.

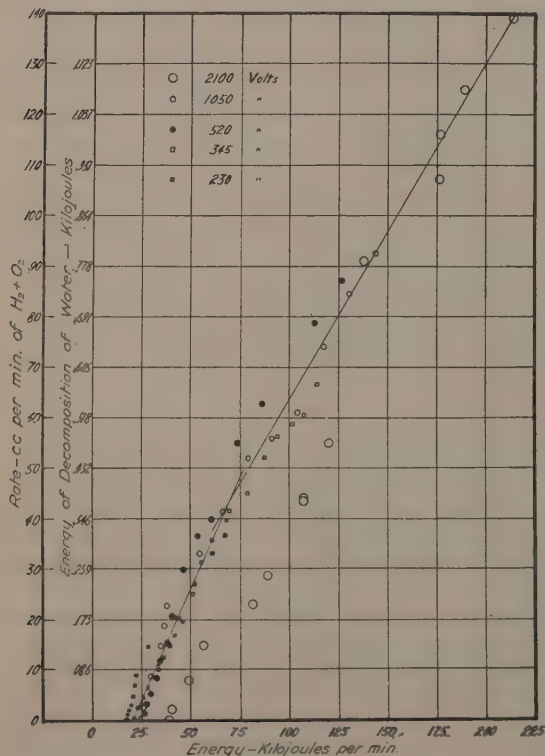


FIG. 14. Relation of the Rate of Decomposition of water to the Rate of Electrical Energy.

The inner vertical scale in Fig. 14 shows the amount of energy used up in decomposing liquid water corresponding to the hydrogen and oxygen produced (calculated considering the heat of formation of H_2O as 69,000 calories). The energy converted into chemical energy was, as is shown in the lower part of the curve, 0.75% of the energy over and above 20 kilojoules

per minute, and in the upper part, 0.56% of the *total* energy. There is therefore a point of critical energy for these electrodes at 20 kilojoules per min. below which decomposition does not take place. Up to the critical energy point, the energy is evidently not great enough to ionize the steam and thus to cause arcing. These figures, as follows from the curves, are only approximate.

RELATION OF CURRENT DENSITY

In order to find out if the rate of decomposition by high voltage arcing, was, as in A. C. electrolysis, related to current density, three series of experiments were performed, with three pairs of electrodes of the same length, but of different diameters. All of these experiments were carried out at 2100 volts and with an alkaline electrolyte at the boiling point. The results are shown in Fig. 15. Although the lines shown represent only in a very limited manner, the points obtained by experiment, it is evident that for a certain current the rate of gas evolution increases as the area of the electrode decreases. In other words, the rate of decomposition increases with the current density.

On the other hand, when the rate in cc. per sq. cm. in place of the observed rate, is plotted against the current density in place of the current in Fig. 15, the order of the three curves becomes reversed, and they become more widely separated. It follows, therefore, that at a constant *current density* the rate of decomposition of the water due to arcing, increases as the diameter of the electrode increases. That this follows from theoretical reasoning will be shown in a further paragraph.

Two points on the curves in Fig. 15 may be worthy of special mention. The maximum rate of gas evolution with electrode diameter 0.203 cm. was 266 cc. per

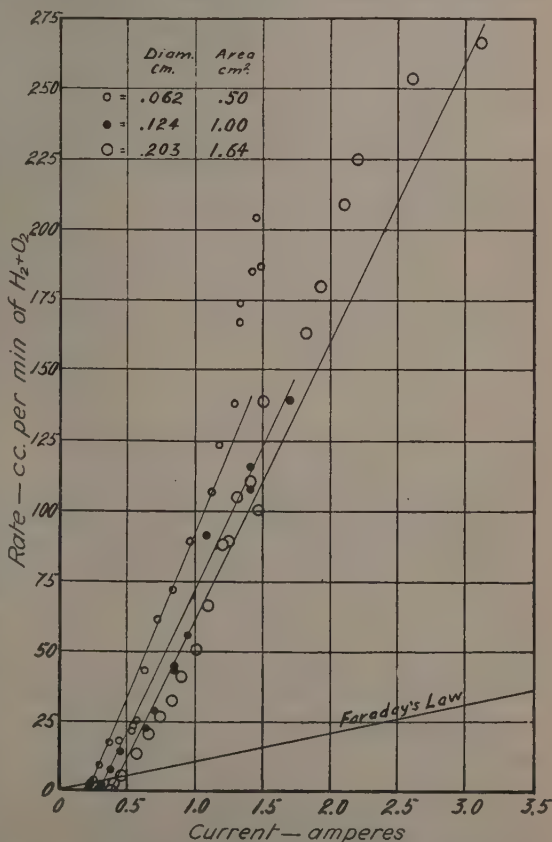


FIG. 15. Rate of Decomposition of water by arcing at 2100 volts with various sizes of electrodes.

minute, which must necessarily be smaller than the true value due to small losses of gas owing to the overloading of the steam condensers. This was the greatest rate measured in these experiments, and represents a value of 826% of that calculated from Faraday's Law for the same current. On analysis it was found to contain by volume 65.0% hydrogen and 30.6% oxygen. Again, the maximum point of the curve with electrode diameter 0.062 cm. represents a value 1350% of that calculated for the same current by Faraday's Law. Analysis of the gas evolved gave approximately the same composition as given above.

INFLUENCE OF TEMPERATURE OF THE ELECTROLYTE

Experiments were performed to find the change in the rate of decomposition at constant atmospheric pressure and constant voltage with change in the average temperature of the electrolyte. Owing to the impossibility of obtaining accurate temperature readings, the values obtained are not given, but sufficient evidence was obtained to show that at constant voltage, pressure and current, the rate of gas evolution increases very rapidly with an increase in the average temperature of the electrolyte. Steam was formed on the electrodes at temperatures in the electrolyte above about 60° C. The rate of gas formation was very low in the absence of steam formation. An increase in the amount of steam formed and in the arcing was observed with an increase of temperature. It therefore seems that the rate of decomposition at high voltages by the electric arc, at other temperatures than the boiling point, is related to the amount of energy actually used in producing steam. In all the experiments conducted at the boiling point the temperature was maintained approximately constant by application of external heat to compensate for loss by radiation.

THE SOLUTION OF IRON

As referred to above, in almost all of the 300 determinations of the rate of decomposition of water by high voltage arcing, carried out in this research, the analyses showed more than twice the volume of hydrogen than oxygen. In addition, below the critical current density of A. C. electrolysis, and below the arcing point, small but appreciable volumes of hydrogen were observed. The diameter of the steel electrodes decreased continually with use. No traces of hydrogen were observed at low currents with a boiling electrolyte, nor at higher currents with a cold electrolyte. It is therefore believed that at higher currents and boiling electrolyte but below the arcing point, electrolytic solution of the iron takes place and hydrogen is thereby produced (or oxygen is consumed).

In the electric arc it is probable that particles of iron are torn off the electrode and react with the electrolyte or with the oxygen to produce the quantities of excess hydrogen observed. This was borne out by an experiment during which the electrode was burned through by the heat of the arc, the gas analysis subsequently showing the volume of hydrogen to be three times the volume of oxygen.

THE ARCING POINT, EFFECT OF VOLTAGE

On increasing the current at high voltages arcing commences at a definite point, the value of which, as is seen in Fig. 13, decreases as the voltage increases. With electrodes exposing an area of one sq. cm., this arcing point was determined over a range from 110 to 4200 volts. The results are shown in Fig. 16. The current at which arcing commences was found to vary inversely as the potential between the electrodes.

Although the rate of decomposition is almost the same for the same energy or power at all voltages, as is seen in Fig. 14, the power at which arcing commences varies with the voltage. The power corresponding to the arcing current is also shown in Fig. 16. Assuming the relation to be represented by the straight line as shown, this relation of the arcing power to the potential will be:

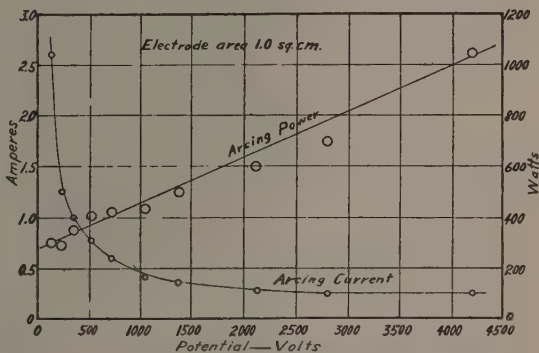


FIG. 16. Relation between the point at which arcing commences and the potential between the electrodes.

$$W = AE + B \quad (11)$$

in which A and B are constants, W is the arcing power in watts, and E the potential. These constants under the conditions and electrodes used above have the values of 0.18 and 280 respectively. The equation for the current curve therefore becomes

$$I_R = A + \frac{B}{E} \quad (12)$$

which, using the above values for A and B , gives the current at which arcing commences over this range of voltages. The values obtained are closely in agreement with the observations. The lower limiting value of the current, or current density in this case, providing the equation continues to hold at higher voltages, is 0.18 amperes.

These equations are of importance in the design of the electric boiler as they show that a greater power per sq. cm. can be used in an electric boiler at high voltages than at low, without arcing taking place on the electrodes. On the other hand, at voltages below 110, arcing has not been found to produce dangerous amounts of electrolytic gases (29).

THE ARCING POINT, EFFECT OF DIAMETER OF ELECTRODES

The point at which arcing commenced with a potential difference of 2100 volts between steel wire electrodes of a length of 2.56 cm., was determined for various diameters of the electrodes. Sodium hydroxide solution, at the boiling

point at atmospheric pressure was used as the electrolyte. The current at which arcing commences increases as the diameter increases, according to a straight line function, as is seen in Fig. 17, which may be represented by the equation

$$I_R = Md + N \quad (13)$$

in which I_R is the arcing current and d the diameter of the electrodes. In the above experimental conditions the constants M and N had the values 0.48 L, and 0.06 L respectively (L being the length of the electrode).

On the other hand the current density at which arcing commences decreases as the diameter increases, according to a hyperbolic function, as is seen in Fig. 17. The equation becomes:

$$I'_R = \frac{.06}{\pi d} + \frac{.48}{\pi} \quad (14)$$

From this it is seen that when the diameter is infinite, that is with a flat surface, the current density at which arcing commences is equal to $\frac{.48}{\pi}$ or 0.153 amperes per sq. cm. Experimentation with small electrodes was limited due to the unavoidable fusion of the wires.

A similarity between the arcing current density curve and the cell constant (or the resistance per unit electrolyte), curve is shown in Fig. 17. The cell constant was determined for each pair of electrodes with N/50 KCl. It was observed that at constant voltage and varying sizes of electrodes, arcing

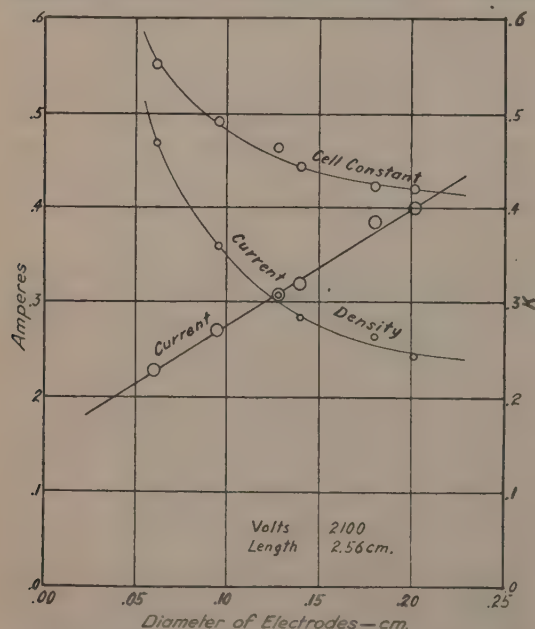


FIG. 17. Relation between the point at which arcing commences and the diameter of the electrode.

commences at the same concentration of the alkaline electrolyte which concentration for 2100 volts was 0.0002 N. This indicates a relationship between the arcing point and the resistance of the cell.

If we assume that the arc takes place from the electrode to the electrolyte through the breaking down of a layer of water or through a steam bubble of a definite thickness, say 1 mm., it is readily seen that the current from a definite area on the electrode will, in the case of the small diameter electrodes, pass through a larger volume of electrolyte to reach the boundary of this layer 1 mm.

distant, than with the larger electrodes. The energy density, in *joules per cubic centimeter*, will therefore be less at the same *current density* and voltage with the small electrodes than with the larger electrodes. We would therefore expect the arcing current density with the small electrodes to be greater than with the large electrodes, as has been found experimentally (Fig. 17.).

In a similar manner the results obtained by converting the points in Fig. 15, to the basis of one sq. cm. as described above, may be explained. The increase in the rate per sq. cm. at constant current density with increase in the diameter of the electrodes follows from the greater energy density with the large electrodes.

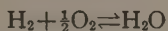
THE EFFECT OF PRESSURE

Experiments were conducted to determine the effect of pressure on the arcing point. The electrodes, protected by rubber stoppers and with heavily insulated leads, were placed in a heavy Pyrex flask, equipped with a pressure gauge, safety valve and steam vent. The concentration of the alkaline electrolyte was maintained constant for each experiment, and the voltage and current raised until arcing commenced with the electrolyte boiling at atmospheric pressure. The apparatus was then closed up and the pressure and temperature allowed to rise.

Twelve experiments were carried out at voltages from 700 to 2200 and in all cases the arcing, which was much in evidence at atmospheric pressure, disappeared entirely when the pressure was increased, notwithstanding the fact that the current increased as the temperature was raised. Three lb. above atmospheric pressure suppressed the arcing at 700 volts, whereas 31 lb. were required to suppress the arcing at 2200 volts. Quantitative measurements could not be made, but sufficient evidence has been obtained to show that pressure elevates the point at which arcing commences.

ELECTRICAL OR THERMAL DECOMPOSITION ?

The decomposition of water vapor by the electric arc leads to the query, "Is the decomposition entirely a thermal decomposition due to the high temperatures obtained in the electric arc, or is it in some way an electrical decomposition ?" The equilibrium



has been studied by Nernst and Wartenberg (24) and by Bjerrum (4), who have determined the degree of dissociation up to 2600° C., at which temperature 10% of the water vapor was found to be dissociated. Similar experiments were carried out by a different method by Holt (14). As such temperatures are readily obtainable by the electric arc, it is conceivable that the water vapor in a bubble through which an arc passes may be raised to a high temperature, and partly decompose, a recombination of the products being prevented by the sudden cooling of the electrolyte.

If we assume that all of the electrical energy, (Fig. 14, produces steam, and that the electric arc passes through all the steam (which approaches the truth at high rates of energy) the percentage of steam decomposed into hydrogen and oxygen is very nearly a constant in the upper part of the curve and has the value, for these particular electrodes, of approximately 0.077%. This equilibrium, if an equilibrium can be considered to have been reached, between



would correspond to a temperature of about 1600° C., according to the results obtained by Nernst and Wartenberg. As the percentage of steam decomposed is a constant, it follows that if the decomposition is purely thermal, the temperature of the arc is a constant and independent of the rate of energy and the electrical pressure. This is possible if we consider that the volume of the arc increases as the energy increases, the concentration of the energy remaining the same. This increase in volume might be accomplished by an increase in the length of the arc.

The fact that ordinary electrolytic decomposition plays a small part, if any, in decomposition by high voltage arcing is evident from the complete independence of the rate of gas evolution from Faraday's Law, as shown in Fig. 13 and Fig. 15. Decomposition of water vapor by the electric spark was observed by Perrot (22) in 1858, who found 20 times as much decomposition in the spark chamber as in a voltmeter. Thomson (32) found certain similarities but a great number of differences between decomposition of water vapor by the electric arc or spark and ordinary electrolysis. The subject of electrolysis of steam, as it is called, has been investigated by Chapman and Lidbury (5), Holt and Hopkinson (15) and by Kernbaum (19), all of whom consider the hypothesis of electrolysis as in liquids inapplicable.

Nevertheless it is conceivable that the rapid flow of electrons in the high potential gradient occurring in the electric arc, might cause the decomposition of water molecules in addition to the decomposition due to the kinetic energy of these molecules. Evidence in favor of electrical decomposition by the current in high voltage arcing is seen by the fact, as mentioned above and as shown in Fig. 14 that at a constant rate of flow of electrical energy, the rate of gas evolution, constant at voltages between 230 and 1050, decreases at voltages of 2100 and 4200. At these high voltages the current is correspondingly less for the same rate of flow of electrical energy, which indicates a relation in this range between the current and the rate of decomposition, or indicates electrical decomposition. At low voltages on the other hand, rapid decomposition by electrolysis takes place and the effect of arcing itself is too small to be isolated.

The explanation of thermal decomposition, despite the probably necessary assumption of a constant arc temperature, is the most simple, but further evidence as to the nature of both types of decomposition is necessary before definite conclusions can be drawn.

VII Practical Applications of the Investigation

The widespread use of the water-resistor type of electric steam generator not only by pulp and paper mills, smelters and commercial plants but also for domestic heating and central heating plants calls for the proper design of heater and boiler to give the best and safest service. Practically nothing was known about the behavior of alternating current in respect to the water electrolyte when this type of heater and boiler was first introduced and the consequence was that these were constructed and operated in such a manner that hydrogen and oxygen were generated in dangerous quantities. The popularity of the electric steam generator, however, demanded its continued manufacture and use. It was found that by operating at low current densities the generation of gases was appreciably diminished while the pressure under which the system operated no doubt reduced the decomposition of the water by arcing.

Many of the electric steam generators now in operation are decomposing considerable quantities of water into hydrogen and oxygen but since these gases are highly diluted with steam at the point of generation there is little danger of ignition until part or all of the steam has condensed. This residual gas must always be viewed with suspicion; minor explosions have occurred where care had not been exercised to sweep out or vent the gases left after the condensation of the steam.

Where steam accumulators are fed from electric steam generators the condensation of the steam will free the residual gases. Consequently these accumulators should be so constructed that the condensation takes place in a separate chamber before the steam enters the accumulator. Otherwise the residual gases will collect above the hot water and may form a highly explosive mixture. The residual gas collecting in the top of the chamber could easily be vented and thus eliminated from the system.

"Air locked" radiators fed from electric steam generators may contain explosive gases and should be vented periodically, avoiding danger of ignition while doing so.

That there have been but few explosions connected with the use of the water-resistor type of electric boiler must be attributed to the improbability of ignition rather than to the absence of an accumulation of explosive gases.

The first principle to be observed in constructing and operating the electric steam generator in order to prevent the decomposition of the water is to attain uniform current density upon the electrodes. The current density used commercially in steam-producing electric boilers is about 0.75 amp. per sq. in. This is the *average* current density and is far below the *critical current density* of 19 amp. per sq. in., but commercial electrodes are not always so constructed that the design or subsequent corrosion may not bring certain areas well above the critical current density; the electrolysis of water therefore follows in accordance with the law of A. C. electrolysis.

The current density over the bare ends of suspended electrodes will always be above the critical current density. Corrosion of such electrodes will proceed from the lower ends. Vertical concentric cylinders insulated above and below, should be adaptable as electrodes in the use of three-phase current.

ELECTRODE MATERIALS

The experimental results indicate that any form of commercial iron or steel may be used in constructing the electrodes. The critical current density for iron and steel is sufficiently high that generators may be operated efficiently, well below the current density at which electrolytic gases are generated. The construction and design of the electrodes should be such that local high current densities cannot be found upon their surface. If the current density is unevenly distributed upon the electrodes then the average current density as calculated from the current flowing and the exposed surface of the electrodes does not ensure that electrolytic gases are not being generated. *Electrolytic gases will appear wherever the current density rises above the critical current density.* All of the current above the critical current density will be utilized in decomposing the water.

A properly constructed boiler could be operated safely at several times the capacity now in common use, if the conditions of uniform current density were incorporated in the design of the electrode chamber.

Copper has a critical current density equal to about half that possessed by iron and steel and should not therefore be used as electrode material. Nickel has a higher critical current density than iron but it is doubtful whether nickel-plated ware would stand up under the conditions of operation within the electrode chamber. Carbon electrodes disintegrate rapidly during A. C. electrolysis and give rise to both carbon monoxide and gaseous hydrocarbons together with hydrogen and oxygen. Aluminum cannot be used as it has an exceedingly low critical current density, probably less than 0.01 amp. per sq. cm. and moreover it corrodes very rapidly.

CORROSION OF ELECTRODES

Iron and steel electrodes were found to corrode under the influence of A. C. electrolysis, the extent of the corrosion being proportional to the current density at low voltages, and to the arcing at high voltages. For the same electrode material the corrosion was uniform when the distribution of current over the electrodes was uniform. Electrodes in commercial generators sometimes corrode very rapidly, and the shape of the electrode soon differs markedly from that of the original installation. The distribution of current over the surface of the electrodes will vary with the alteration in shape. Irregular or non-uniform corrosion of the electrodes is indicative of irregular distribution of the current.

GASES GENERATED

The A. C. electrolysis of water above the critical current density with metallic electrodes should give equivalent quantities of hydrogen and oxygen. Analysis of gases collected from commercial installations rarely show such

proportions unless the evolution of the gases is rapid. This discrepancy is due to three possible causes. First, corrosion of the electrodes and of the electrode chamber permits the iron to react on the water chemically, releasing an excess of hydrogen. Second, oxygen is absorbed in the formation of the hydroxides of iron and consequently is removed from the system. Thus it is usual to find an excess of hydrogen over that of oxygen in the residual gases. Moreover the ordinary corrosion of iron anywhere in the system may give rise to further evolution of hydrogen and absorption of oxygen. The third factor affecting the composition of the gases is the removal of the dissolved gases in the feed waters. These, if natural waters, are saturated with atmospheric gases which are driven out of solution at the temperature of the electrode chamber.

ARCING IN COMMERCIAL BOILERS

Commercial installations operating under high voltages will invariably produce electrolytic gases unless the pressure is sufficient within the electrode chamber to prevent the formation of steam bubbles. It has been found that arcing decomposed the water into hydrogen and oxygen in a quantity several times that possible from electrolytic decomposition alone. When boilers operate at voltages of 6,600 or higher this decomposition may be ten or twenty times that produced by the current even if all of the current flowing was utilized in the electrolysis of the water. Arcing on the electrodes with its accompanying thermal decomposition of water is no doubt the cause of most of the explosive gases generated by high voltage operation.

The ideal installation, if mechanically and economically possible, would make provision for heating the water electrically under considerable pressure, below the boiling point and for passing it into a second chamber where it could boil at a lower pressure. Pressure inhibits steam formation and prevents arcing since this takes place across bubbles of steam. The safe current carrying capacity of the electrodes could be greatly increased if steam formation were prevented.

The formation of bubbles of steam upon the surface of the electrodes no doubt forms an insulating layer which reduces the actual surface in contact with the electrolyte and raises the current density on local areas. This may be a contributory cause to the decomposition of the water.

HOT WATER HEATERS

The automatic operation of hot water heaters of the water-resistor type with submerged electrode makes the heaters particularly attractive for domestic heating. The earlier forms of heaters no doubt favored the decomposition of the water, but with the fundamental knowledge of A. C. electrolysis made available by this research, it should be possible to design and construct heaters that would operate without the danger of generating and igniting explosive gases. The critical current density is the limiting factor in the designing of such heaters operating on 60-cycle, 110-volt circuit. Higher frequencies raise

the critical current density and are thus more desirable. Higher voltages, on the other hand, introduce the element of arcing and the possibility of thermal decomposition of the water. Hot water heaters, even when possessing automatic valve vents, should be provided with a glass gauge to indicate the water level inside the electrode chamber. The operator could then observe any accumulation of residual gases within the electrode chamber.

EXPLOSION HAZARD

There is a tendency on the part of mill operators and the manufacturers of electric steam generators and heaters to minimize the danger from explosion due to gases formed by the decomposition of water. This tendency is reprehensible. As already pointed out, high voltage operation of steam generators accompanied by arcing decomposes relatively large quantities of water into its elements. There is little or no danger of explosion within the generator itself as the evolution of steam sweeps the electrolytic gases out of the electrode chamber. The danger of an explosion lies wherever the steam condenses, if the residual gases can become trapped or mixed with air. As mentioned before, there is usually a considerable excess of hydrogen over oxygen. In fact in the gases collected at some distance from the generator, there is sometimes very little oxygen. When mixed with air, however, this residual gas may form an explosive mixture.

The range of explosiveness for mixtures of hydrogen and oxygen is very great as may be seen from Table II. Moreover the steam present does not inhibit the possibility of ignition and explosion any more than do other inert gases. The collection of residual gases within the electrode chamber was not prevented in the early hot water heaters of the water-resistor type and ignition was provided by arcing on the electrodes or from the electrodes to the water when surging exposed the lower end of either one or the other electrode.

The engineer in charge of an electric steam generator may easily ascertain the presence of explosive gases in steam by cooling at some convenient point to condense the steam. The residual gas can then be tested for inflammability and explosiveness. Accumulated residual gases anywhere in the system should be so tested from time to time. If the residual gases are found to be inflammable or explosive, it may be assumed that the generator is decomposing water either by alternating current electrolysis or arcing or both.

Acknowledgments

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STUDIES ON THE ACTION OF SULPHATES ON PORTLAND CEMENT

II. STEAM-CURING OF PORTLAND CEMENT MORTAR
AND CONCRETE AS A REMEDY FOR SULPHATE
(ALKALI) ACTION¹BY T. THORVALDSON², V. A. VIGFUSSON³ AND
D. WOLOCHOW³

Abstract

A study was made of the effect of steam-curing at various temperatures between 50° and 200° C. on the resistance of Portland cement mortars to the action of solutions of the sulphates of sodium, magnesium and calcium. The methods used consisted in comparing the expansion of steam-cured and untreated mortar specimens during exposure to the solutions, and in determining the changes in the tensile strength of the more resistant mortars after long periods of exposure.

A laboratory study of steam-curing as a remedy for the action of sulphates ("alkali") on Portland cement mortars, was made by determining the effect on the stability of the mortar as indicated by changes in volume and in tensile strength on exposure to sulphate solutions at 21° C. The effect of steam-curing on the tensile and compressive strength of mortars and concrete was also studied.

Introduction

Observations on the increased resistance of concrete cured in steam at 100° C. to the disintegrating action of the so-called "alkali water" were first published in 1924 by D. G. Miller (1) who described experiments on concrete cylinders. The results of a two-year study of the effect produced on the resistance of Portland Cement mortars to sulphate action by curing in steam and water at temperatures of 100° C. and less, have already been published from this laboratory (4). Measurements of the expansion of steam-cured mortars in solutions of sodium and magnesium sulphates indicated that the increase in resistance of the specimens towards the action of solutions of sodium sulphate is much more marked than in the case of magnesium sulphate solutions. Further, a microscopic study of the changes taking place in Portland cement mortars during steam-curing at temperatures between 100° and 200° C. (3) indicates that free lime gradually disappears, while a new crystalline substance is formed; also that these crystals are very stable in solutions of sodium and calcium sulphate but are decomposed slowly by solutions of magnesium sulphate. It therefore appears probable that the formation of these crystals during curing in steam is connected with the increased resistance of the mortar to the action of sulphates.

Evidently further investigation was necessary to determine the conditions of steam-curing best adapted to increase the resistance to the action of sulphates, and to yield a mortar, or concrete, of high tensile and compressive strength. Such a study is most effectively carried out in the laboratory where every condition such as temperature, concentration and purity of the sub-

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stances used can be controlled. However, the findings of the laboratory investigation should be subsequently tested by field experiments. This article describes further extensive laboratory studies with this purpose in view.

Experimental Methods

When dealing with normal Portland cements it has been found possible to follow the progress of the action of solutions of sulphates on sand mortars and concrete by means of measurements of the linear expansion of the specimens; it has also been shown that the loss in strength of the material can be estimated approximately from the linear expansion (2,5). Since this method is very convenient on account of the relatively few test pieces required even when many variables are involved, it is chiefly used in this study for measuring the effect of the sulphate solutions on the steam-cured specimens. However, it is not possible to assume with certainty that the effect of the steam-curing of mortars will influence in the same way or to the same degree the rate at which the specimens expand and that at which they lose strength in sulphate solutions. On this account, therefore, a number of determinations of tensile strength are also carried out. The expansion and loss in strength are thus treated as separate variables affecting the stability of the mortar.

For the determination of tensile and compressive strength, briquets and cylinders were made according to the standard methods. The mortar bars ($.625 \times .625 \times 7.5$ in.) selected for the determination of the rate of expansion and of the tensile strength were made from cement and standard Ottawa sand in the proportion, by weight, indicated. Distilled water was used for gauging. The specimens were cured in a damp closet or in distilled water, as stated. The amount of mixing water employed was generally the same as that specified by the standard methods for 1:3 standard-sand briquets. All the work was carried out at 21° C. in a constant humidity room to ensure uniformity in the specimens.

The length of the bars was measured by means of a micrometer head set in a steel frame and graduated to read to 0.0001 in. The bars were made with a thin layer of neat cement on each end to form a smooth bearing surface and make measurements of length reproducible. They were exposed to the action of the solutions in closed sealers in constant temperature rooms at 21° C. Three 1:5 mortar bars were placed in 1,700 cc. or four 1:10 bars in 1,650 cc. of the sulphate solution.

The measurements of the tensile strength of the mortar bars were made by means of a special clamp consisting of two parts, each corresponding in shape and size to one-half of a broken standard briquet. The clamp, with the piece of mortar bar firmly held in it, was inserted into the standard clip of an Olsen Cement Tester and the tension measured in the same way as that of an ordinary briquet. As the cross section of the bar was a square only 0.625 in. at the side, the experimental value obtained for the tensile strength was multiplied by the factor 2.56 to convert it to lb. per sq. in.

Description of the Portland Cements Used

The results of physical tests made on the cements used are given in Tables I and II, and the chemical analyses in Table III.

TABLE I
PHYSICAL TESTS ON CEMENTS*

Sample No.	Through sieve 200 mesh per in. per cent	Normal consistency per cent	Soundness in steam	Time of setting (Gillmore)	
				Initial	Final
126	88.1	24	O.K.	2 hr 40 min.	6 hr 25 min.
326	83.4	22	O.K.	3 hr 45 min.	6 hr 15 min.
826	86.4	23	O.K.	4 hr 15 min.	8 hr 25 min.
127	90.8	25	O.K.	2 hr —	4 hr 5 min.
427	82.0	24	O.K.	4 hr 30 min.	8 hr 20 min.
428	82.8	24	O.K.	2 hr 10 min.	4 hr —

*The authors are indebted to Professor G. M. Williams of the Department of Civil Engineering of the University for the physical tests given in Tables I and II.

TABLE II
TENSION AND COMPRESSION TESTS*

Time in Days	Cement No. 126	Cement No. 326	Cement No. 826	Cement No. 127	Cement No. 427	Cement No. 428
Tensile strength in lb. per sq. in.						
1	—	—	—	230	—	—
3	—	275	—	320	—	—
7	265	305	285	375	310	315
28	420	415	410	435	420	—
Compressive strength in lb. per sq. in.						
7	1295	2740	1980	3085	2280	—
28	2540	3185	2810	3785	3110	—

*The tension tests were carried out on 1:3 standard-sand briquets and the compression tests on 1:3 standard-sand cylinders (2 × 4 in.).

TABLE III
CHEMICAL ANALYSIS OF CEMENTS

Cement No.	SiO ₂ per cent	Al ₂ O ₃ per cent	Fe ₂ O ₃ per cent	CaO per cent	MgO per cent	SO ₃ per cent	Loss on ignition per cent
126	22.22	6.83	1.89	63.39	2.45	1.97	1.49
326	20.02	6.97	2.61	63.48	3.86	1.85	1.25
826	21.91	6.11	2.52	61.22	3.84	1.84	2.10
127	19.26	7.00	2.87	62.61	4.00	2.73	1.55
427	20.78	7.20	2.18	61.54	3.61	2.00	2.22
428	23.95	5.58	2.16	63.42	2.04	1.59	0.71

Expansion of Mortar Bars during Steam-Curing

The expansion which took place during the steam-curing of mortars varied materially with the age of the specimen, with the time of the treatment and with the temperature; it was also found to differ for Portland cements from different sources.

Mortar bars cured in steam contract slightly for some time after they have been cooled to room temperature. The first measurements of the bars, after the treatment, were usually made after 24 hours, but while most of the contraction had taken place by that time, it continued slightly for several days. Data on the expansion of 1:5 and 1:10 bars on curing in saturated steam at various temperatures are given in Tables IV and V. The values given represent averages of a very large number of bars.

TABLE IV
RELATIVE EXPANSION DURING STEAM-CURING

For varying times at 100° C. ¹		For 24 hr at various temperatures ²	
Time of exposure to saturated steam at 100° C.	Linear expansion per cent	Temperatures of saturated steam	Linear expansion per cent
2 hr	0.000	100	0.030
6 hr	0.003	110	0.048
12 hr	0.007	125	0.056
24 hr	0.017	150	0.07
3 days	0.020	175	0.16
5 days	0.024		
10 days	0.028		

¹ Cement No. 126; mix 1:5, age of bars at time of steam-curing 7 days.

² Cement No. 427; mix 1:10, age of bars at time of steam-curing 11 days.

TABLE V
RELATIVE EXPANSION OF VARIOUS CEMENTS CURED IN STEAM*

Cement No.	Age in days of mortar before steam-curing	Linear expansion per cent
826	7	0.035
326	11	0.037
127	9	0.056
427	11	0.070

* Mix 1:10; temperature of steam 150° C.; time of steam-curing 24 hours.

The first two columns of Table IV indicate that with the duration of curing in saturated steam at 100° C. there is a progressive increase in the expansion which apparently approaches a maximum. Seven-day old bars of mix 1:10,

made from the same cement (No. 126), gave, after curing in saturated steam at 100° C. for ten days, an average expansion of 0.032% which is slightly higher than that of the 1:5 mix.

Columns 3 and 4 of Table IV show that as the temperature of saturated steam is raised the expansion increases gradually until a temperature is reached at which there is a rather sudden increase in the expansion. For cement No. 427 this sudden increase occurs between 150° and 175° C. This excessive expansion is probably related to the decrease in strength of specimens cured in steam at high temperatures.

The comparison of the four Portland cements made in Table V indicates that the expansion of mortar specimens prepared from different cements varies considerably. Thus the specimens made from cement No. 427 expanded twice as much during a 24-hour treatment at 150° C. as similar specimens made from No. 826.

Effect of Curing Mortars in Water-vapor at Temperatures below 100° C. on their Resistance to Sulphates

New experiments with 1:5 mortar bars cured in water-vapor at 50°, 75° and 85° C. confirmed previous results (2). Curing for one to ten days in saturated water-vapor or water at 50° C. very slightly increased the rate of expansion of the bars in solutions of sodium and magnesium sulphate. Similar treatment at 75° C. was found to have a slight retarding effect on the rate of expansion in the same solutions, while curing the mortar in saturated water-vapor at 85° C. for five or ten days rendered the mortar much more stable in these solutions. Curing of Portland cement mortars in water-vapor at temperatures below 100° C. cannot, however, be considered as a practical method for increasing the resistance of the mortar to sulphate action on account of the loss in strength of the mortar produced by the treatment (2). Under severe climatic conditions such loss in strength probably more than counterbalances any advantage due to decreased action of the sulphate on the cement.

Effect of Curing in Steam at 100° C. on the Resistance of Mortars to Sulphate Action

A brief summary of expansion tests made with 1:5 bars prepared from cement No. 126 and cured in saturated steam at 100° C. for periods of time varying from two hours to ten days, is given in Table VI. The solutions used were 0.15M. (2.1%) and 0.50 M. (6.7%) sodium sulphate, 0.15M. (1.8%) and 0.50 M. (5.7%) magnesium sulphate. The time required for various linear expansions is also reported.

TABLE VI
EFFECT OF CURING IN STEAM AT 100°C. ON RATE OF EXPANSION OF PORTLAND CEMENT MORTAR BARS IN SULPHATE SOLUTIONS

EFFECT OF CURING IN STEAM AT 100° C. ON RATE OF								
Duration of steam-curing	None	2 hours	6 hours	12 hours	24 hours	3 days	5 days	10 days
Time to produce given expansion								
Linear expansion per cent								
A. In 0.15 M. Na ₂ SO ₄								
0.01	1 day	4 days	5 days	3 days	9 days	21 days	12 months	26 months
0.02	4 days	6 days	9 days	13 days	13 days	10 months	20 months	3.5 years
0.05	7.5 days	10 days	14 days	20 days	5 months	26 months	3.5 years	
0.10	9 days	13 days	18 days	49 days	16 months	4 years*		
0.20	11.5 days	15 days	25 days	6 months	3.5 years			
0.50	14 days	19 days	36 days	21 months				
1.00	16 days	24 days	54 days					
B. In 0.50M. Na ₂ SO ₄								
0.01	1 day	2 days	4 days	8 days	11 days	12 days	2 months	13 months
0.02	3.5 days	7 days	13 days	16 days	30 days	7 months	14 months	21 months
0.05	6.5 days	16 days	21 days	36 days	6 months	2 years	2 years*	3 years
0.10	8.5 days	21 days	27 days	2 months	13 months	2.5 years	4 years*	
0.20	11 days	29 days	33 days	4.5 months	19 months	3.5 years		
0.50	15 days	39 days	45 days	14 months	3 years			
1.00	19 days	50 days	2 months	3 years				
C. In 0.15 M. MgSO ₄								
0.02	3 days	2 days	5 days	4 days	5 days	3 days	6 days	3 days
0.05	8 days	8 days	10 days	11 days	15 days	26 days	27 days	30 days
0.10	10 days	10 days	13 days	16 days	26 days	68 days	3.5 months	3 months
0.20	12 days	12 days	17 days	19 days	43 days	4 months	11 months	11.5 months
0.50	15 days	16 days	24 days	44 days	3.5 months	23 months	3.5 years	5 years*
1.00	18 days	23 days	40 days	3.5 months	15 months	0.6% in 3 years		
D. In 0.50 M. MgSO ₄								
0.01	1 day	2 days	3 days	3 days	2 days	3 days	3 days	5 days
0.02	2.5 days	3 days	4 days	4 days	4 days	6 days	5 days	8 days
0.05	5 days	5 days	7 days	7 days	8 days	14 days	10 days	14 days
0.10	6.5 days	7 days	9 days	10 days	11 days	24 days	19 days	29 days
0.20	8.5 days	8.5 days	11.5 days	13.5 days	19 days	48 days	2 months	3 months
0.50	10.5 days	11 days	16 days	22 days	35 days	5.5 months	13 months	17 months
1.00	13 days	17 days	25 days	45 days	3.5 months	22 months	3 years	5 years*

*Estimated.

NOTE: Cement No. 126; mix 1:5 (11.8% water); bars 7 days old when placed in steam.

The effects of the treatment on the rate of expansion in solutions of the two sulphates differ so markedly that they will be considered separately. While bars cured two hours in steam at 100°C. show a slight decrease in the rate of expansion in solutions of sodium sulphate, the effect is not marked until after the bars have been thus treated for twelve hours. There is a further rapid decrease in the rate of expansion with increased duration of treatment up to five days, after which the mortar appears to be very resistant to the action of solutions of sodium sulphate. Treatment for an additional period of five days has a relatively much smaller effect on the rate of expansion. The bars cured in steam for 24 hours or more appear to be in perfect condition at the end of 3.5 years.

The steam treatment does not prevent the expansion of the bars exposed to the action of magnesium sulphate to the same extent, although the expansion of bars cured in steam at 100°C. for 24 hours or more is very materially retarded. Curing for ten days at 100°C. lengthens the time required for an expansion of 0.5% in 0.15 M. MgSO_4 almost 120 times, and that required for the same expansion in 0.50 M. MgSO_4 nearly 50 times. At the end of 3.5 years the bars are covered with a white deposit, and all except those cured five or ten days in steam show other slight signs of deterioration.

In Table VII the tensile strength of the mortar bars described in Table VI after 3.5 years exposure to the solutions, is compared with the tensile strength of the same bars at the time they were placed in the solutions.

TABLE VII
TENSILE STRENGTH OF MORTAR BARS DESCRIBED IN TABLE VI*

Duration of steam-curing at 100°C.	Tension in lb. per sq. in.				
	Initial	After 3.5 years exposure to:			
		0.15 M. Na_2SO_4	0.50 M. Na_2SO_4	0.15 M. MgSO_4	0.50 M. MgSO_4
12 hours	85	110	103	225 ^a	
24 hours	85	100	240	235 ^b	
3 days	100	100	180	295	220 ^c
5 days	110	115	160	290	315
10 days	130	95	110	305	365

NOTE: Elongation: (a) 2.7%, (b) 1.2%, (c) 1.2%.

*After exposure to sulphate solutions for 3.5 years.

A comparison of the results given in Tables VI and VII shows that the tensile strength of the specimens varies independently of the expansion.

The tension of the bars in 0.15 M. Na_2SO_4 has not changed much from its initial value at the time of immersion. In 0.50 M. Na_2SO_4 there is considerable increase in strength except for the bars cured ten days in steam; while this period of steam-curing is most favorable to the lowering of the rate of expansion, it apparently also causes a decrease in strength in solutions of sodium sulphate. On the other hand, all the bars cured in steam at 100°C . for twelve hours or more increased in strength when immersed in solutions of magnesium sulphate, the largest increase corresponding to the longest period of steam-curing. The behavior of the bars cured for shorter periods indicates that ultimately these bars will begin to lose strength, bend and develop cracks.

For comparison it may be stated that similar mortar bars stored in water instead of steam, for ten days, and then exposed to sulphate solutions lose from 75 to 90% of their tensile strength in 14 to 15 days in 0.15 M. Na_2SO_4 , 0.50 M. Na_2SO_4 and 0.15 M. MgSO_4 ; in 0.50 M. MgSO_4 , the same effect is produced in ten days.

The cause of the increased resistance to sulphate action brought about by steam-curing must be considered. It might be suggested that it decreases the permeability of the specimens on account of increased hydration and gel formation, or that it stabilizes some reactive components in the hydrated cement against the chemical action of the sulphate. The former suggestion apparently does not fully explain the result since factors which decrease the permeability, such as an increase in the richness of mortar, lower the rate of expansion in solutions of magnesium sulphate more than in solutions of sodium sulphate (2), while the effect of steam-curing is the reverse.

A study of the behavior of extremely lean steam-cured bars when exposed to sulphate solutions gives further evidence on this question. Bars made of one part of cement to ten parts of standard sand are extremely permeable to sulphate solutions but are strong enough for use if handled carefully.

Table VIII gives a comparison between the rates of expansion of 1:5 and 1:10 mortar bars, made from cement No. 126, when exposed to 0.15M. solutions of sodium and magnesium sulphate; it gives a similar comparison for bars which had been cured in saturated steam at 100°C . for ten days. All bars in both lots were seven days old when exposed to steam and were kept continually in the damp chamber except during the period of steam-curing. The 1:5 bars were 28 days old and the 1:10 bars 19 days old when exposed to the sulphate solutions.

TABLE VIII
RELATIVE RATE OF EXPANSION OF 1:5 AND 1:10 MORTARS
IN SULPHATE SOLUTIONS*

Linear expansion per cent	In 0.15 M. Na ₂ SO ₄		In 0.15 M. MgSO ₄	
	Mix 1:5	Mix 1:10	Mix 1:5	Mix 1:10
A. Bars cured in damp closet at 21° C.				
0.01	1 day	1 day	1 day	1 day
0.02	4 days	3 days	3 days	2 days
0.05	7.5 days	5 days	8 days	4 days
0.10	9 days	7 days	10 days	6 days
0.20	11.5 days	8.5 days	12 days	8 days
0.50	14 days	11 days	15 days	10 days
1.00	16 days	13 days	18 days	15 days
B. Bars cured ten days in steam at 100° C.				
0.01	26 months	15 months	1 day	1 day
0.02	3.5 years	0.013% in 26 months	3 days	5 days
0.05			30 days	8 days
0.10			3 months	18 days
0.20			11.5 months	64 days
0.50			0.26% in 3 years	8 months
1.00				0.62% in 26 months

*All mortars were made with cement No. 126.

From Table VIII it appears that the 1:10 mortar bars, steam-cured for ten days at 100°C. develop, in a 0.15 M. solution of sodium sulphate a stability which is comparable to that attained by the 1:5 mortar bars on similar treatment. It seems therefore that the permeability of the test pieces plays here only a minor role, and that the curing in steam stabilizes the hydrated cement against the action of sodium sulphate solutions. In the 0.15 M. solution of magnesium sulphate, on the other hand, the rate of expansion of the 1:10 bars is much more rapid than that for the 1:5 bars, indicating that here permeability plays a more important part. The very marked slowing up of the expansion of the 1:10 steam-cured bars, as compared with that of the untreated bars shows, however, that the resistance of the hydrated cement to the action of magnesium sulphate has been increased materially by curing in steam.

Effect of Concentration on Rate of Expansion

In Table IX is given a comparison of the rates of expansion at 21°C. of 1:10 mortar bars, both untreated and steam-cured, in solutions of sodium and magnesium sulphate of various concentrations, and in a saturated solution of calcium sulphate. The bars were seven days old when exposed to steam at 100°C. for ten days, and were 19 days old when immersed in the sulphate solutions.

TABLE IX

RELATIVE RATES OF EXPANSION OF UNTREATED AND STEAM-CURED MORTAR BARS IN SOLUTIONS OF Na_2SO_4 AND MgSO_4 OF VARIOUS CONCENTRATIONS AND IN SATURATED CaSO_4 SOLUTION*

Linear expansion per cent	Concentration of Na ₂ SO ₄ solution					Concentration of MgSO ₄ solution					Concentration of CaSO ₄ solution
	0.05M. 0.70%	0.15M. 2.09%	0.50M. 6.70%	1.00M. 12.70%	saturated 17%	0.05M. 0.60%	0.15M. 1.77%	0.50M. 5.70%	1.00M. 10.82%	saturated 26%	saturated 0.21%
	Time for given expansion										
A. Bars cured in damp closet 19 days											
0.01	3 days	1 day	<1 day	<1 day	<1 day	<1day	<1day	<1 day	<1 day	<1 day	5 days
0.02	5 days	3 days	1.5 days	1.5 days	1.5 days	2.5 days	2 days	1.5 days	2 days	1 day	10 days
0.05	8 days	5 days	3.5 days	3.5 days	3.5 days	6 days	4 days	2.5 days	3 days	1 day	24 days
0.10	10.5 days	7 days	5 days	6 days	6 days	8 days	6 days	2.5 days	4 days	1.5 days	39 days
0.20	15 days	8.5 days	11 days	10 days	10 days	11 days	8 days	3.5 days	5 days	2.5 days	55 days
0.50	82 days	11 days	45 days	45 days	45 days	15 days	10 days	5.5 days	7.5 days	3.3 days	92 days
1.00	123 days	13 days	96 days	96 days	96 days	24 days	15 days	8 days	7.5 days	3.3 days	120 days
B. Bars cured in damp closet 9 days and in saturated steam at 100°C. 10 days											
0.01	>26 months	15 months 0.013% in 26 months	10 months	8 months	5 months	1 day	1 day	1 day	1 day	>26 months	>26 months
0.02		20 months 0.024% in 26 months	20 months 0.025% in 26 months	20 months 0.025% in 26 months	15 months	5 days	5 days	2 days	1 day		
0.05				26 months	26 months	36 days 0.073% in 26 months	8 days	4 days	2 days		
0.10						18 days	18 days	5.5 days	2.5 days	<1 day	
0.20						64 days	64 days	8 days	3 days	1.2 days	
0.50						8 months 0.62% in 26 months	8 months	15 days	5 days	2 days	
1.00						27 days	27 days	27 days	7.5 days	3 days	

*Cement No. 126, mix 1:10 (10.5% water)

It is evident when considering the effect of concentration on the expansion of the untreated bars (A in Table IX) that there is a marked difference between this effect in sodium sulphate solutions and that in magnesium sulphate solutions. In solutions of magnesium sulphate the rate of expansion increases progressively with concentration, while in solutions of sodium sulphate the highest rate of expansion occurs in the 0.15 M. solution. The rate of expansion is lower both for solutions of concentration 0.05M. and 0.50M. or higher. This is quite general for lean mortars made from Portland cements although cements of low resistance to the action of sodium sulphate usually behave the same way in solutions of Na_2SO_4 as of MgSO_4 (2).

From the results of the expansion of the steam-cured bars given under B in Table IX, it appears that the 1:10 mortar bars are extremely stable in all concentrations of sodium sulphate, although there is a slight progressive increase in the rate of expansion with concentration. Yet the expansion in 1.0M. (12.7%) solution of sodium sulphate at 21°C. is only equivalent at the end of two years to the expansion which would take place on raising the temperature of the specimen about 30°C. The steam treatment is effective in stabilizing the 1:10 mortar also against the action of a saturated solution of calcium sulphate. On the other hand, the effect of concentration is very marked with solutions of magnesium sulphate. Thus while steam-curing for 10 days at 100°C. increases materially the resistance of the mortar to 0.05M. and 0.15 M. solutions of magnesium sulphate¹, there is no appreciable difference between the rate of expansion of the treated and the untreated bars in 1.0 M. and in saturated solutions of this salt.

It must be remembered, however, that these results are obtained with extremely lean mortars and that, in practice, ground waters containing a concentration of MgSO_4 higher than 0.15 M. are not common. The situation is therefore not as serious as it appears. As the richness of mix of the steam-cured mortar increases, producing greater impermeability, the stability also shows an enormous relative increase. Thus, a 1:5 standard-sand mortar (Table VI) which is still a rather permeable material as compared with rich concrete made with well graded aggregate, expands as shown in Table X.

TABLE X
RELATIVE RATES OF EXPANSION OF TREATED AND UNTREATED 1:5 MORTARS
IN SOLUTIONS OF MgSO_4

Concentration of MgSO_4 solutions	Expansion per cent	Time for given expansion		Time-ratio of steam-cured to untreated bars
		Untreated bars	Bars cured in steam 10 days at 100° C.	
0.15M.	0.2	12 days	11.5 months	30
	0.5	15 days	5 years	120
0.50M.	0.2	8.5 days	88 days	10
	0.5	10.5 days	17 months	50

¹ It takes the 1:10 steam-cured bars more than 120 times as long to expand 0.10% of their length in 0.05 M. MgSO_4 and 24 times as long to expand 0.5% in 0.15 M. MgSO_4 as the untreated bars.

Tensile strength tests were made on the steam-cured mortar bars described under B in Table IX after exposure for 28 months to the sulphate solutions. The bars in the three most concentrated solutions of magnesium sulphate had disintegrated by this time. For purposes of comparison it might be stated that the tensile strength of the untreated bars has usually dropped to 0.1 or less of its initial value when the bars reach a linear expansion of between 0.5 and 1%.

TABLE XI
TENSILE STRENGTH OF 1:10 STEAM-CURED MORTAR BARS*

Concentration of solution	Tensile strength in lb. per sq. in.	Concentration of solution	Tensile strength in lb. per sq. in.
0.05 M. Na_2SO_4	38	0.05 M. MgSO_4	56
0.15 M. Na_2SO_4	23	0.15 M. MgSO_4	73
0.50 M. Na_2SO_4	49	Saturated CaSO_4	56
1.00 M. Na_2SO_4	46		
Saturated Na_2SO_4	51		

*After exposure to the sulphate solutions at 21° C. for 28 months.

NOTE: Cement No. 126, mix 1:10 (10.5% water). The bars were placed in saturated steam at 100° C. when nine days old and cured in steam for ten days. The tensile strength of 1:10 mortar briquets treated in the same way was 63 lb. per sq. in. 24 hours after the end of the period of steam-curing.

From Table XI it appears that there has been a considerable loss in strength of the steam-cured specimens during 28 months exposure to solutions of sodium sulphate, more particularly in the case of those exposed to the dilute solutions. It is not possible to make a comparison with bars stored 28 months in the same volume of distilled water since no untreated or steam-cured bars were available in this series for this purpose.

Effect of Curing in Saturated Steam at Various Temperatures on the Tensile Strength of Standard-Sand Mortar Briquets

The loss in strength of mortar specimens cured in steam at 100°C. seems to be the most serious obstacle to the use of steam-curing at that temperature as a remedy for sulphate action. Concrete of low strength, saturated with alkali water, is likely to fail when exposed to low winter temperatures. Under conditions found in practice where the structural material undergoes extreme seasonal changes in temperature, the factor of strength becomes an important one in determining the resistance to disintegrating influences such as sulphate action. On the other hand, it is well known that Portland cement mortars cured in saturated steam under pressure normally develop high strength (3, 6). It seems therefore possible that steam-curing at temperatures above 100°C. will meet the difficulty, if no other injurious effects are introduced. Hence, further experiments were made with a number of different Portland cements to determine the effect, on the tensile strength of mortar specimens, of curing in saturated steam at temperatures between 100° and 200°C. Some of the results obtained have already been published (3) and additional results are given in Fig. 1 and 2.

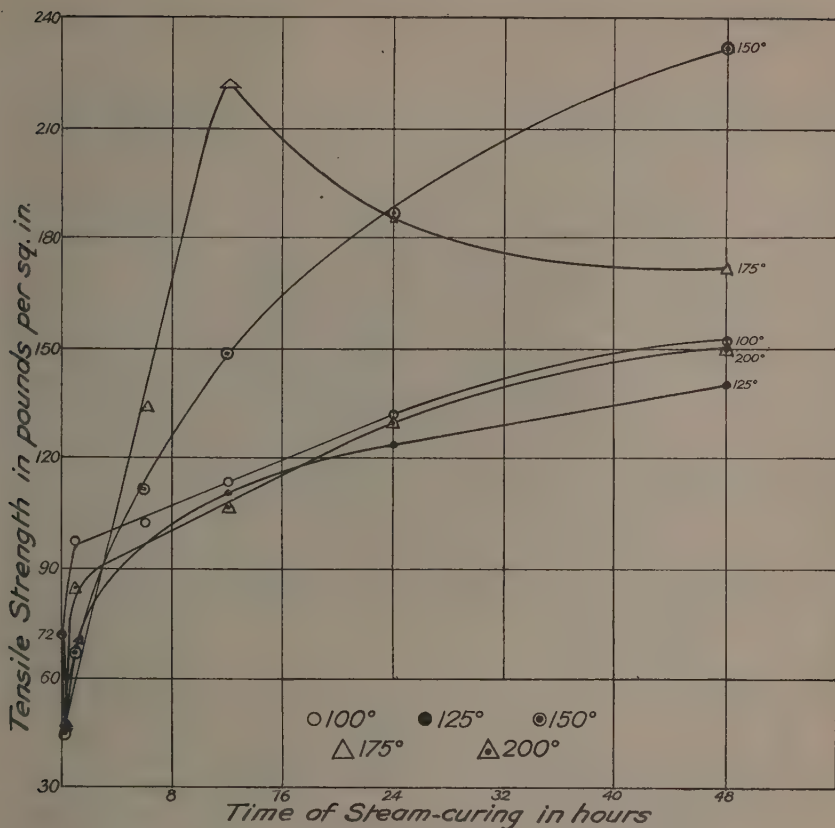


FIG. 1. Effect of Steam-curing on the Tensile Strength of Two-day Briquets.

All curing in steam under pressure was done in gas-heated autoclaves, the specimens being protected as far as possible from direct contact with water. The temperature was controlled only approximately but may in general be assumed to have been within 2° to 3°C. of the temperature given, while variations of 5°C. for short intervals of time occurred occasionally.

The results obtained with two-day old 1:5 standard-sand mortar briquets of cement No. 826 at temperatures between 100° and 200°C. are plotted in Fig. 1 and the corresponding results obtained with briquets which were 28 days old when steam-cured in Fig. 2. Each point represents the average for three or four specimens.

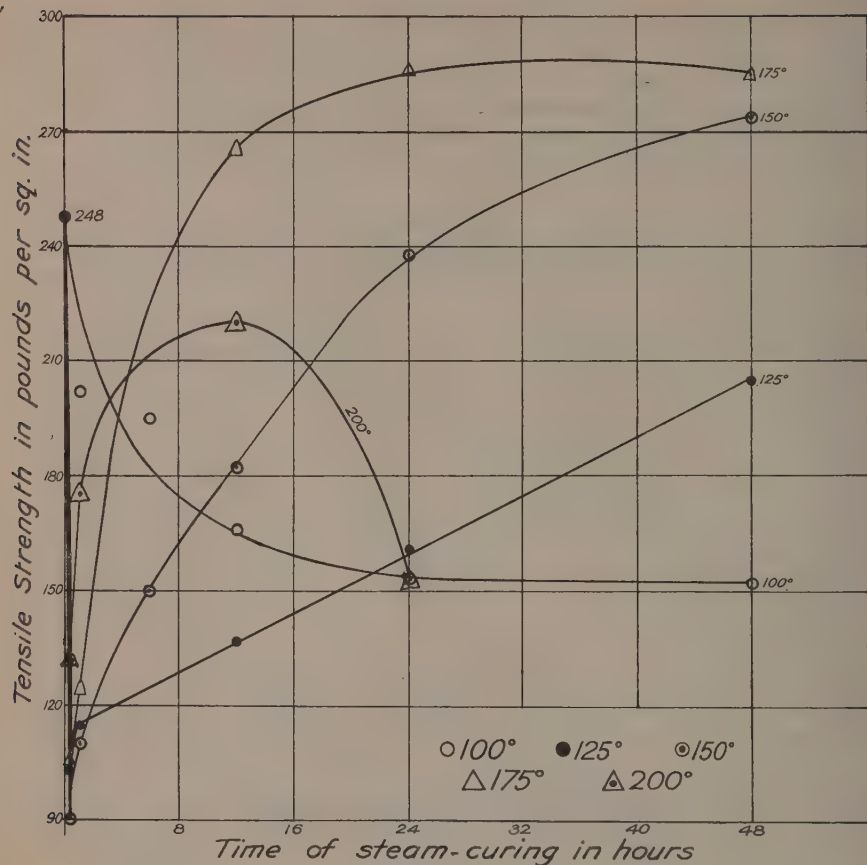


FIG. 2. Effect of Steam-curing on the Tensile Strength of 28-day Briquets.

While after steam-curing there is initially a marked loss of tensile strength of the mortar specimens, a considerable increase soon follows, the rate of increase varying as the temperature of steam-curing. For the higher temperatures of curing the tensile strength soon reaches a maximum beyond which it generally decreases. Thus the optimum temperature varies with the time of steam-curing. For very short periods, temperatures between 175° and 200°C. appear to produce the greatest increase in strength, while for periods of more than 12 hours temperatures of 150° to 175°C. give the most favorable results.

Effect of Curing in Saturated Steam at Various Temperatures on the Compression of 2×4 in. Concrete Cylinders¹

The concrete cylinders used in these experiments were made from a batch of the following composition: Cement No. 428, 1815 gm; sand, 7000 gm.; gravel

¹ The cylinders and the tension tests were made by the Civil Engineering Laboratories of the University of Saskatchewan.

(0.25 in. to 0.375 in.), 7000 gm; water, 1577 gm.; flow (15 bumps), 170; weight 0.05 cu. ft.) 2533 gm.

One lot of cylinders was cured in steam when two days old, the second lot when 28 days old. The compression tests were made when the specimens were four days old and 30 days old. Each value recorded was the mean for three to six specimens. The values obtained for the compressive strength are given in Table XII and represented graphically in Fig. 3 and Fig. 4.

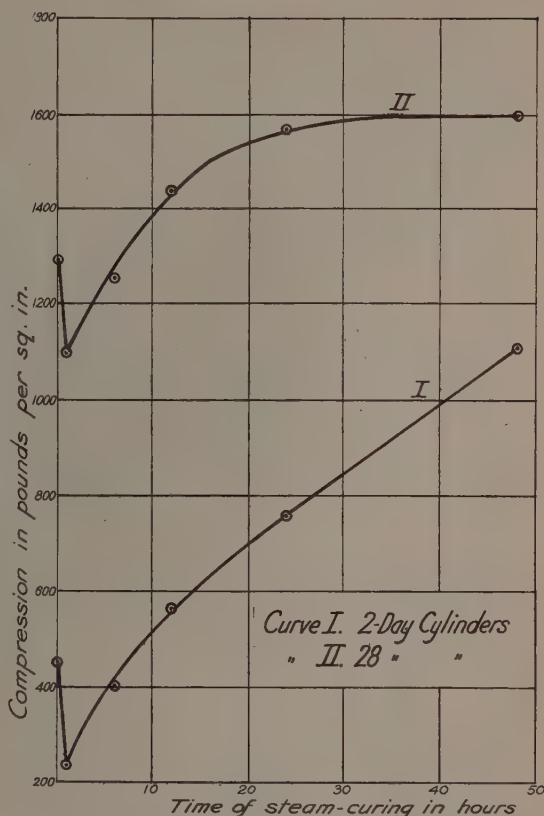


FIG. 3. Effect on Compressive Strength of Steam-curing at 150° C.

TABLE XII

EFFECT OF STEAM-CURING ON COMPRESSION

Temperature of steam-curing	Time of steam-curing	Compression 2-day specimens in lb. per sq. in.	Compression 28-day specimens in lb. per sq. in.
—	None	315 (2-day)	
—	None	455 (4-day)	1295 (28-day)
100°C.	24 hours	615	1380
125°	24 hours	690	1690
150°	24 hours	760	1570
175°	24 hours	1195	1290
200°	24 hours	1090	
150°	1 hour	240	1100
150°	6 hours	405	1255
150°	12 hours	565	1440
150°	24 hours	755	1570
150°	48 hours	1110	1600

The compression of both the 2-day and 28-day specimens decreases when they are cured in saturated steam at 150° C. for short periods of time (Fig. 3). On continued treatment the 2-day cylinders show a rapid progressive increase in compression with the duration of the treatment up to 48 hours, the maximum time used. The 28-day specimens also increase in compression but the rate is very slow after the first 24-hour period.

The curves in Fig. 4 indicate that on curing for periods of 24 hours at

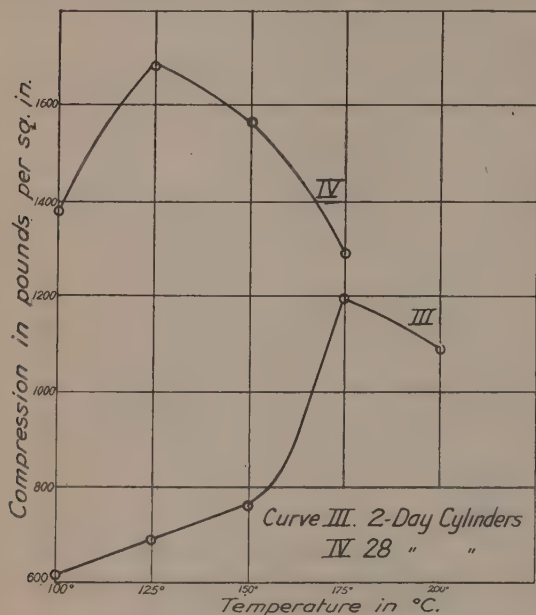


FIG. 4. Effect of Curing for 24 Hours in Saturated Steam at Various Temperatures.

various temperatures, the compression at first increases with rise in temperature, but that an optimum temperature is soon reached. The temperature giving the maximum compression is lower for the 28-day than for the 2-day specimens, and for the cement used, the 2-day specimens cured 24 hours at 175° C. have almost as high a compression as the 28-day specimens cured similarly. Other experiments show that the optimum temperature varies with different cements, so that each individual cement should be studied in order to find the conditions producing the highest strength.

Effect on the Resistance to Sulphate Action of Curing in Saturated Steam under Pressure

The rapid increase in both tensile and compressive strength of mortar specimens when cured in saturated steam at temperatures above the boiling point of water, suggested that, by selecting a suitable temperature, the time of steam treatment necessary to produce a certain definite degree of resistance to sulphates might be cut down very materially; also, that the extra advantage of high strength might be obtained. Further studies were therefore undertaken in connection with the effect of steam-curing at various temperatures for different lengths of time on the rate of expansion, and on the change in tensile strength of specimens immersed in sulphate solutions.

Effect of Temperature of Steam-Curing

The expansion, in 0.15 M.Na₂SO₄, 0.15 M.MgSO₄ and in saturated CaSO₄ solutions, of 1:10 mortar bars made of cement No. 427 and cured in saturated steam at temperatures between 100° and 175° C. is given in Table XIII; the changes in tensile strength of the specimens in Table XIV. The bars were exposed to steam when 11 days old and after the steam treatment were stored in water till 28 days old, being then immersed in the sulphate solutions.

TABLE XIII

RELATIVE EFFECT ON EXPANSION PRODUCED BY STEAM-CURING 1:10 MORTAR BARS
AT VARIOUS TEMPERATURES*

Linear expansion per cent	Temperature of steam-curing					
	21°C.	100°C.	110°C.	125°C.	150°C.	175°C.
A. In 0.15 M.Na ₂ SO ₄						
0.01	1 day	3 days	3 months	3 months	7 months	No expansion in 12 months
0.02	3 days	10 days	12 months	12 months	12 months	
0.05	5.5 days	7 months				
		0.07% in 12 months				
0.10	7 days					
0.20	8.5 days					
0.50	10.5 days					
1.00	12.5 days					
B. In 0.15 M.MgSO ₄						
0.02	1 day	1 day	1 day	1 day	2 days	2 days 7 days 65 days 0.14% in 12 months
0.05	3 days	3 days	7 days	5 days	5 days	
0.10	5 days	13 days	30 days	25 days	25 days	
0.20	6.5 days	32 days	65 days	2.5 months	5 months	
			0.46% in 12 months	0.38% in 12 months	0.24% in 12 months	
0.50	8.5 days	10 months				
1.00	11.5 days					
C. In saturated CaSO ₄						
0.01	3 days	7 days	12 months	12 months	5 months	No expansion in 12 months
0.02	7 days	18 days			12 months	
0.05	11 days	9 months				
		0.06% in 12 months				
0.10	13.5 days					
0.20	15.5 days					
0.50	20 days					
1.00	25 days					

*The curing was done in saturated steam for 24 hours.

NOTE: Cement No. 427; mix 1:10 (10.3% water); age in days at time of steam curing 11, at time of immersion in sulphate solution 29; time of steam-curing 24 hours.

TABLE XIV

TENSILE STRENGTH OF STEAM-CURED MORTAR BARS AFTER EXPOSURE TO SULPHATE SOLUTIONS
AT 21°C. FOR 12 MONTHS*

Temperature of steam-curing	Tension at time of exposure to solutions in lb. per sq. in.	Tension (in lb. per sq. in.) after 12 months exposure		
		in 0.15 M. Na ₂ SO ₄	in 0.15 M. MgSO ₄	in saturated CaSO ₄
100°C.	44	46	102	35
110	40	46	123	54
125	41	55	128	54
150	60	56	159	57
175	89	72	143	71
200 (10 hours only)		87	190	64

*Cement No. 427; mix 1:10 (10.3% water). The bars when 11 days old were cured in saturated steam at various temperatures for 24 hours; then stored in distilled water till 28 days old and exposed to sulphate solutions.

The results given in Tables XIII and XIV indicate that the expansion of the mortar in sulphate solutions is progressively retarded as the temperature of steam-curing increases; also that the increase of tensile strength of the specimens, after 12 months exposure, is generally of the same order as that of the temperature of the steam treatment. The cement used has a very low resistance to sulphate action and produces a mortar of abnormally low tensile strength when steam-cured for 24 hours. The great increase in resistance produced by steam-curing at 175°C. especially in 0.15 M. MgSO₄ is rather interesting since it has been found (3) that this temperature is the most favorable for the formation in the mortar of a crystalline product which is very resistant to the action of sulphates.

Effect of Time of Steam-Curing at 150°C.

A comparison is given in Table XV of the effect of steam-curing, for various periods of time in saturated steam at 150°C., on the expansion of mortar bars in solutions of 0.15M., 0.50M. and 1 M. Na₂SO₄, 0.05, 0.15 and 0.50M. MgSO₄ and in a saturated solution of CaSO₄. The corresponding effect on tensile strength is given in Table XVI. The bars were made from cement No. 826, and a 1:10 mix; they were steam-cured when seven days old, and immersed in the sulphate solutions when 11 days old. This cement had a very high resistance to sulphate action.

TABLE XV

EFFECT OF TIME OF STEAM-CURING AT 150°C. ON EXPANSION IN SULPHATE SOLUTIONS*

Linear expansion per cent	Time of steam-curing				
	None	1 hour	6 hours	24 hours	72 hours
A. In 0.15 M. (2.09%) Na ₂ SO ₄					
0.01	4 days	40 days	45 days	10 months	20 months
0.02	6 days	10 months	12 months	20 months	
0.05	8.5 days	0.03% in 20 months	0.03% in 20 months		
1.00	26 days				
B. In 0.50 M. (6.7%) Na ₂ SO ₄					
0.01	4 days	1 month	1 month	10 months	20 months
0.02	5 days	10 months	10 months	20 months	
0.05	9 days	0.03% in 20 months	0.03% in 20 months		
1.00	43 days				
C. In 1.00 M. (12.7%) Na ₂ SO ₄					
0.01	2 days		1.5 months	2.5 months	20 months
0.02	5 days	not determined	12 months	20 months	
0.05	9 days		0.03% in 20 months		
1.00	77 days				
D. In 0.05 M. (0.60%) MgSO ₄					
0.01	1 day	1 day			1 day
0.02	2 days	3 days	1 day	1 day	3 days
0.05	7 days	25 days	10 days	12 days	28 days
		0.09% in 20 months	0.08% in 20 months	0.08% in 20 months	0.08% in 20 months
0.10	11 days				
1.00	2.5 months				
E. In 0.15 M. (1.77%) MgSO ₄					
0.01	1 day				1 day
0.02	2 days	1 day	1 day	1 day	3 days
0.05	6 days	7 days	7 days	6 days	7 days
0.10	8 days	34 days	1.5 months	1.5 months	1.5 months
0.20	11 days	2.5 months	4 months	9 months	15 months
			0.41% in 20 months	0.30% in 20 months	0.23% in 20 months
0.50	17 days	7 months			
		0.70% in 20 months			
1.00	31 days				
F. In 0.50 M. (5.70%) MgSO ₄					
0.01				1 day	3 days
	not determined	not determined			
0.02			1 day	2 days	5 days
0.05			3 days	5 days	8 days
0.10			7.5 days	11 days	15 days
0.20			13.5 days	29 days	30 days
0.50			27 days	70 days	53 days
1.00			46 days	3.5 months	3 months
G. In saturated CaSO ₄					
0.01	11 days		2.5 months	7 months	8 months
		not determined			0.15% in 20 months
0.02	20 days		12 months	20 months	
			0.03% in 20 months		
0.05	40 days				
1.00	7.5 months				

*Cement No. 826; mix 1:10 (10.3% water). Bars exposed to sulphate solutions when 11 days old.

TABLE XVI

TENSILE STRENGTH OF MORTAR BARS CURED IN STEAM AT 150°C. FOR VARIOUS PERIODS OF TIME*

Time of steam-curing	Tension in lb. per sq. in.						
	Before exposure to solutions	After exposure for 20 months					
		in 0.15M. Na ₂ SO ₄	in 0.50M. Na ₂ SO ₄	in 1.00M. Na ₂ SO ₄	in 0.05M. MgSO ₄	in 0.15M. MgSO ₄	in saturated CaSO ₄
1 hr	18	48	52	—	72	110	—
6 hr	28	64	94	76	102	116	68
24 hr	86	86	73	155	110	131	45
72 hr	123	144	132	177	187	120	55

NOTE: Cement No. 826; mix 1:10 (10.3% water).

*When 11 days old the bars were exposed to sulphate solutions at 21°C. for 20 months. Tensile strength of similar briquets 11 days old, 54 lb. per sq. in., after exposure to distilled water for 20 months, 82 lb. per sq. in.

Examination of Tables XV and XVI indicates that with increased duration of steam treatment up to the maximum time used (72 hours), there is, in general, a progressive increase in retardation of expansion and a progressive increase in tensile strength both before and after exposure to the solutions for 20 months. This is true of all bars except those exposed to saturated solutions of calcium sulphate.

Comparison of the Efficiency of Steam-Curing at 100° and 150°C.

It is evident as is seen in Table XIII that the 24-hour treatment at 150°C. is much more efficient than the similar treatment at 100°C. The results given in Tables IX, XIII and XV indicate that steam-curing for 24 hours at 150°C. is approximately as effective as curing for ten days at 100°C. in retarding expansion in solutions of sodium and calcium sulphate, but more effective in retarding expansion in solutions of magnesium sulphate. From Tables XI, XIV and XVI it is apparent that the shorter treatment at the higher temperature is superior in preventing loss of strength in sulphate solutions except possibly in the saturated calcium sulphate solutions. These results, however, were obtained with Portland cements from different mills. Tables XVII and XVIII contain a direct comparison between the effect of curing 1:10 bars of cement No. 326 five days in steam at 100°C., and 24 hours in saturated steam at 150°C.

TABLE XVII

RELATIVE EFFECT OF CURING FIVE DAYS IN STEAM AT 100° C. AND 24 HOURS
IN STEAM AT 150°C. ON EXPANSION IN SULPHATE SOLUTIONS

Linear expansion per cent	Time required for given expansion				
	in 0.15 M.Na ₂ SO ₄	in 0.50 M.Na ₂ SO ₄	in 0.15 M.MgSO ₄	in 0.50 M.MgSO ₄	in saturated CaSO ₄
A. Bars cured in damp closet 15 days					
0.01	4 days	4 days	2 days	1 day	8 days
0.02	6 days	5 days	3.5 days	2 days	10 days
0.05	7 days	7 days	5.5 days	3 days	11 days
0.10	8 days	9 days	7 days	3.5 days	12 days
0.20	9 days	10 days	9 days	5 days	14 days
0.50	11 days	13 days	11 days	7 days	17 days
1.00	12 days	16.5 days	14 days	9.5 days	21 days
B. Bars cured in damp closet 10 days; in steam at 100°C. 5 days					
0.01	1 day				1 day
0.02	1.5 months	1 day	1 day		20 months
0.05	0.03% in 20 months	17 months	3 days	1 day	
0.10		0.06% in 20 months	23 days	2.5 days	
0.20			2 months	4.5 days	
0.50			18 months	8 days	
1.00				15 days	
C. Bars cured in damp closet 14 days; in steam at 150° C. 24 hours					
0.01	8 months	3 months	1 day	1 day	4 months
0.02	0.015% in 20 months	8 months	2 days	2 days	20 months
0.05		0.03% in 20 months	9 days	5 days	
0.10			2 months	10 days	
0.20			5 months	20 days	
0.50			0.33% in 20 months	37 days	
1.00				57 days	

NOTE: Cement No. 326; mix 1:10 (10.2% water). The bars were steam-cured when nine days old and exposed to sulphate solutions when 15 days old.

TABLE XVIII

RELATIVE EFFECT OF CURING FIVE DAYS IN STEAM AT 100° C. AND 24 HOURS IN STEAM AT 150° C.
ON THE TENSILE STRENGTH OF BARS EXPOSED TO SULPHATE SOLUTIONS*

Time of steam-curing	Tension in lb. per sq. in.					
	Before exposure to solutions	After exposure for 20 months				
		in 0.15M. Na ₂ SO ₄	in 0.50M. Na ₂ SO ₄	in 0.15M. MgSO ₄	in saturated CaSO ₄	in distilled water
5 days at 100° C.	77	30	42	80	39	59
24 hr. at 150° C.	83	82	75	190	72	

*Cement No. 326; mix 1:10 (10.2% water). Bars exposed to sulphate solutions when 15 days old.

It appears from Table XVII that curing one day in steam at 150°C. is much more effective in preventing expansion in solutions of sodium and magnesium sulphate than curing five days in steam at 100°C. The results in Table XVIII indicate that the advantage of the shorter period at 150°C. is still greater when the effect on the tensile strength of mortar bars of this cement during exposure to solutions of the three sulphates is considered.

Relative Effect of Steam-Curing on Cements from Different Mills

A comparison of the results obtained for mortars treated similarly, but made from different Portland cements, shows certain variations in their behavior in different sulphate solutions. Table XIX gives the relative expansion of 1:10 mortar bars made from Portland cements from four different mills, when exposed to solutions of the sulphates of sodium, magnesium and calcium and Table XX the relative expansion of similar 1:10 mortar bars which had been cured in steam at 150°C. for 24 hours.

TABLE XIX

RELATIVE EXPANSION IN SULPHATE SOLUTIONS OF UNTREATED MORTARS MADE FROM PORTLAND CEMENTS FROM DIFFERENT MILLS

Linear expansion per cent	Cement No. 826	Cement No. 326	Cement No. 427	Cement No. 127
	Time of curing in damp closet			
	11 days	15 days	28 days	15 days
A. In 0.15 M. Na_2SO_4				
0.01	3 days	4 days	1 day	1 day
0.02	6 days	6 days	3 days	3 days
0.05	10 days	7 days	5.5 days	5 days
0.10	14 days	8 days	7 days	6.5 days
0.20	20 days	9 days	8.5 days	7.5 days
0.50	30 days	11 days	10.5 days	9 days
1.00	42 days	13 days	12.5 days	10.7 days
B. In 0.50 M. Na_2SO_4				
0.01	2 days	4 days		1 day
0.02	5 days	5 days		3 days
0.05	10 days	7 days		5 days
0.10	14 days	9 days		6.5 days
0.20	20 days	10 days		8.5 days
0.50	27 days	13 days		12 days
1.00	35 days	16.5 days		16 days
C. In 0.15 M. MgSO_4				
0.01	1 day	2 days		
0.02	3 days	3.5 days	1 day	1 day
0.05	7 days	5.5 days	3 days	3 days
0.10	9 days	7 days	5 days	4 days
0.20	12 days	9 days	6.5 days	5 days
0.50	18 days	11 days	8.5 days	6.5 days
1.00	33 days	14 days	11.5 days	9.5 days
D. In 0.50 M. MgSO_4				
0.01	1 day	1 day		
0.02	2 days	2 days		1 day
0.05	4 days	3 days		1.5 days
0.10	4.5 days	3.5 days		2 days
0.20	6.5 days	5 days		3.5 days
0.50	9.5 days	7 days		4.5 days
1.00	14 days	9.5 days		6 days
E. In saturated CaSO_4				
0.01	11 days	8 days	3 days	6 days
0.02	20 days	10 days	7 days	9 days
0.05	40 days	11 days	11 days	11 days
0.10	68 days	12 days	13.5 days	13 days
0.20	4 months	14 days	15.5 days	18 days
0.50	6 months	17 days	20 days	27 days
1.00	7.5 months	21 days	25 days	37 days

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